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NON-DESTRUCTIVE TESTING TECHNIQUES  
FOR LIQUID PROPELLANTS (U)

B. E. Dawson

June 1967

Air Force Rocket Propulsion Laboratory  
Air Force Systems Command  
Edwards, California

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THIOKOL CHEMICAL CORPORATION  
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Denville, New Jersey

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FOR LIQUID PROPELLANTS (U)

Bruce E. Dawson

June 1967

Air Force Rocket Propulsion Laboratory  
Air Force Systems Command  
Edwards, California

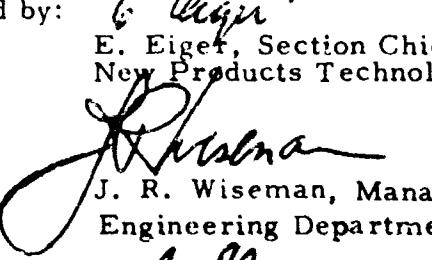
Contract No. AF04(611)-11610

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Reaction Motors Division  
Denville, New Jersey

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**FOREWORD**

This is the final report covering the work performed by Thiokol Chemical Corporation, Reaction Motors Division, Denville, New Jersey under Air Force Contract No. AF04(611)-11610. The internal report number is Report RMD 5808-F. This work was administered under the direction of Sgt. E. Maznicki, Project Engineer, Air Force Rocket Propulsion Laboratory, Air Force Systems Command, Edwards, California.

The research effort reported herein was conducted during the period from 9 May 1966 to 8 May 1967 on Thiokol-RMD Project 5808. The Project Leader was Mr. R. Gere and the Principal Investigator was Mr. B. Dawson. Other contributors to the program were Mr. J. Christakos on the thermal conductivity measurements, Mr. H. Francis on the prototype evaluation, and Dr. A. Beardell, Dr. H. Rubin and Mr. F. Hoffman.

This report contains classified information extracted from other classified documents.

This technical report has been reviewed and is approved.

EDWARD MAZNICKI, TSgt, USAF  
Project Engineer

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(Unclassified Abstract)

**ABSTRACT**

The principal degradation modes for a variety of storable liquid propellants have been identified as thermal decomposition of fuels into gaseous products and tank wall interaction of the oxidizers. Nondestructive testing techniques selected to monitor the propellant degradation included strain gage instrumentation to measure pressure buildup due to decomposition of fuels, pulse-echo ultrasonic technique for corrosion and wall reduction due to oxidizer interaction resulting in system degradation, and a thermal conductivity cell to detect propellant leakage.

The selected techniques were experimentally evaluated with simulated modes of degradation to develop prototype equipment which was used to monitor 27 tanks of propellant under various environmental conditions for three months. Propellants included Compound A, MHF-5 simulated oxidizer of dilute sulfuric acid to accelerate corrosion and simulated fuel of alcohol to permit a more rigorous program of temperature shocks, vibration, and high moisture conditions to accelerate strain gage deterioration.

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I

INTRODUCTION

Existing missile systems utilizing storable liquid propellants exhibit a high degree of reliability which is assured by monitoring the critical hardware components. Propellant monitoring of the missile systems has been based on removing a sample from each propellant tank. The sampling process may not obtain representative samples and could possibly allow contaminants to enter the missile tankage and further degrade the propellants and the system. Also, packaged liquid powerplant configurations are hermetically sealed to eliminate any possibility of powerplant leakage during the long term missile storage, so propellant sampling is not possible since they have no provisions for propellant access. Non-destructive test techniques, which are independent of the missile and are adaptable to field inspection over a wide environmental range, are desirable to monitor the liquid propellants and the effects on the system during their storage life of five years or longer.

The principal problems in applying NDT to packaged liquid propellants are (1) definition of the potential degradation of the propellant, (2) means of detecting the potentially unreliable system, and (3) possible physical manifestation of the degradation as it influences overall system performance. Perhaps the greatest problem lies in the conception of detection methods which are amenable to a missile system. An air launch packaged liquid powerplant (PLP) is basically a sealed "ordnance round" which is mass produced in large quantities. NDT methods for this application should therefore be totally independent of the round and adaptable to field inspection via a portable, easy-to-use instrument and not an internal or integral part of the propulsion system which adds complexity and test components unreliability to the problem. NDT systems must also be operable over a wide environmental range. For conditioned applications, such as a silo launched missile, the restraints are somewhat relieved because of the constant temperature level and the fixed orientation (vertical) of the missile. Mobile launch adds additional restraints but air launch restraints are most exacting.

Thiokol Chemical Corporation, Reaction Motors Division, has investigated the feasibility of techniques which could provide instantaneous information on propellant or system degradation in liquid rocket propulsion systems under Air Force Contract AF04(611)-11610. The program was accomplished in two phases:

Phase I consisted of an analytical investigation to identify liquid propellant degradation and investigate potential non-destructive techniques.

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Phase II consisted of an evaluation of available techniques for detecting liquid propellant or system degradation, the selection of optimum techniques, and the design, fabrication and evaluation testing of a feasibility demonstration prototype non-destructive testing unit. The propellants tested were MHF-5/Compound A.

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**UNCLASSIFIED****II****SUMMARY**

The Phase I, Analytical Investigation, surveyed four oxidizers and six fuels commonly used for high energy liquid propellant systems to determine their physical characteristics and their behavior under long term storage conditions in specific types of tankage materials. The chemistry of these propellants are discussed in detail and the effects of thermal decomposition, corrosivity, and contaminants on these propellants are presented, together with tabulations of physical properties and compatibility with both aluminum and stainless steel alloys based on data in the literature. From this survey, the type and degree of degradation of the propellants was utilized to determine the non-destructive testing techniques applicable to each propellant.

Phase I also included a survey to determine non-destructive testing methods available to measure the anticipated degradation effects, i.e., material thinning, sludging, gas evolution, corrosion and propellant property changes. The applicability of these detection methods to the various modes of degradation and specific detection techniques for Compound A and MHF-5 are listed in appropriate tables. As a result of Phase I, the pulse-echo ultrasonic technique was chosen to monitor tank wall condition for the Compound A oxidizer and strain gage measurements were selected for the internal tank pressures generated by the decomposition of MHF-5. Also, although not an NDT technique per se, development of a thermal conductivity device would permit detection of pin-hole leaks through tankage or tank liners.

The three selected testing methods were evaluated under Task I of Phase II to develop the optimum techniques for their application to monitoring propellants. The intent of this program was to demonstrate the feasibility of using NDT techniques for liquid propellants. Due to limitations in time and funds, techniques could not be fully optimized and existing commercial equipment was utilized rather than developing specialized equipment.

Principally for use with oxidizers, test items were fabricated for use with the pulse-echo ultrasonic equipment manufactured by Branson Instruments, Inc. The utility of the concept for determination of wall thickness and detection of flaws, corrosion, sludge formation, gas evolution, ullage boundaries, and foreign materials was demonstrated.

For fuels, small test tanks fabricated from 2024 aluminum were gaged to evaluate various types of strain gages, adhesives, and waterproofing compounds under the rigorous environmental requirements of this program. The best materials and techniques were selected for the next phase of the program.

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Following a literature survey of leak detection devices, a thermal conductivity cell from Gow-Mac was used to detect Compound A and MHF-5 vapors in concentrations from 30 to 24000 ppm. The cell demonstrated both good sensitivity and selectivity between the two propellants.

Based on all these tests, a test plan for the Phase II, Task II prototype evaluation was submitted and approved by the Air Force. The test plan is incorporated in Appendix C of this report.

For the prototype evaluation, a total of 16 aluminum tanks and 11 stainless steel tanks was fabricated, cleaned, assembled, instrumented and loaded with various propellants. The instrumentation was for both the strain gage and ultrasonic equipment. The propellants included Compound A, MHF-5, and simulated propellants consisting of dilute sulfuric acid to accelerate corrosion and alcohol to permit a more rigorous program of temperature shocks, vibration and high moisture conditions to accelerate strain gage deterioration.

The 27 tanks were stored for a 90 day period with daily monitoring of the liquids. At the conclusion of the test program, the tanks were emptied and cut apart and the contents were analyzed to correlate the condition of the liquids and tanks with the indications received from the NDT measurements. The NDT techniques were successfully demonstrated for the propellant monitoring application.

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## III

**PHASE I, ANALYTICAL INVESTIGATION**

The objectives of this program were to investigate the feasibility of the techniques that will provide rapid and reliable data on propellant or tankage conditions in liquid rocket propulsion systems and to perform the initial feasibility demonstration testing. In conducting the analytical investigation, consideration was given to the following areas:

1. The propellants involved and their degradation modes.
2. The environmental conditions encountered during the storage period and the airborne conditions.
3. The application restraints applied to potential NDT techniques.

The environmental conditions affect both the severity of the propellant degradation and the useful life of the NDT equipment.

**A. Propellant Degradation**

The propellants considered in the analytical investigation are shown in Table I (pg 6) where they are identified by name, chemical composition and governing military specification. The chemical behavior of these fuels and oxidizers under long term storage conditions was studied using existing literature references. The detailed physical properties, chemical reactions, and compatibilities with tank materials of interest are included as Appendix A of this report. Tankage materials considered have been limited to the 1000, 2000, and 7000 series aluminums, 300 series stainless steel, and titanium.

Propellant degradation can occur in three general forms: (1) decomposition to less energetic species, either thermally or through catalytic action with impurities or container materials; (2) reaction with tank walls or impurities; (3) reaction with servicing system materials, including purge or pressurization materials. In general, hydrazine-based fuels are most sensitive to the first form of degradation, whereas both types of oxidizers may be subject to all three degradation modes. Hydrazine-based fuels generally yield only gaseous or liquid products, whereas oxidizers are capable of generating coatings, sludges, and solutions of salts in addition to gaseous products.

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TABLE I  
PROPELLANTS STUDIED IN ANALYTICAL INVESTIGATION

Name	Chemical Composition	MIL-SPEC
Hydrazine	N <sub>2</sub> H <sub>4</sub>	MIL- P- 26536 B
Unsymmetrical Dimethyl Hydrazine	(CH <sub>3</sub> ) <sub>3</sub> NNH <sub>2</sub>	MIL- P- 25604 C
Monomethyl Hydrazine	(CH <sub>3</sub> ) HNNH <sub>2</sub>	MIL- P- 27404
Aerozine-50	50% N <sub>2</sub> H <sub>4</sub> -50% UDMH	MIL- P- 27402
Mixed Hydrazine Fuel-3	N <sub>2</sub> H <sub>4</sub> MMH	MIL- P- 81342 (WP)
Mixed Hydrazine Fuel-5	N <sub>2</sub> H <sub>4</sub> MMH- N <sub>2</sub> H <sub>5</sub> NO <sub>3</sub>	No. N. A. Preliminary Only
Hydrogen Peroxide	H <sub>2</sub> O <sub>2</sub>	MIL- P- 16095 D
Nitrogen Tetroxide	N <sub>2</sub> O <sub>4</sub>	MIL- P- 26539 B
Chlorine Trifluoride	CTF	MIL- P- 24711 Preliminary
Pressurization Gases (Nitrogen)	N <sub>2</sub>	MIL- P- 27401 B
Compound A	ClF <sub>5</sub>	MIL- P- 27413 Preliminary

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The result of any of these degradation modes will have specific effects which may be monitorable. Figure 1 (pg 8) shows schematically more specific types of degradation. These effects are:

## (1) Wall interaction

- (a) generation of gaseous products
- (b) reduction of wall thickness
- (c) formation of solids which settle as sludge
- (d) formation of wall film

## (2) Self-decomposition

- (a) generation of gaseous products
- (b) compositional changes in the liquid
- (c) formation of solids

## (3) Physical transformation

- (a) phase separation
- (b) viscosity change.

These potential changes or effects have been listed in Table II (pg 9), together with the propellants of interest, which allows an assessment of the possibility of each specific propellant undergoing the postulated mode of degradation. This evaluation is based on the propellant survey which is included as Appendix A to this report. The numbers in the table rate the propellant/degradation effect with (1) denoting a severe degradation mode, (2) a moderate mode and (3) indicating that a negligible effect can be expected. This table provided the basis for selecting the appropriate NDT techniques for each propellant, based on its most critical degradation modes, as explained in Section III.C.

It was concluded from the analytical investigation that thermal decomposition problems are experienced with hydrazine-based fuels and hydrogen peroxide, but not with nitrogen tetroxide or interhalogen oxidizers. Decomposition reactions produce high gas evolution rates which are accelerated by metals or atmospheric oxygen with hydrazine-based fuels and hydrogen peroxide. The hydrazine fuels will not attack the tankage.

All oxidizers will attack tankage to a greater or lesser degree although acceptable compatibility characteristics are observed for storage of oxidizers in aluminum and, to a lesser degree, for H<sub>2</sub>O<sub>2</sub> in stainless steel. Corrosion of tankage walls with N<sub>2</sub>O<sub>4</sub> is accompanied by gas evolution and corrosion by interhalogen oxidizers also induces some increase in pressure. The presence of moisture within a tank or propellant wall greatly accelerates the corrosivity reaction by forming strong acids.

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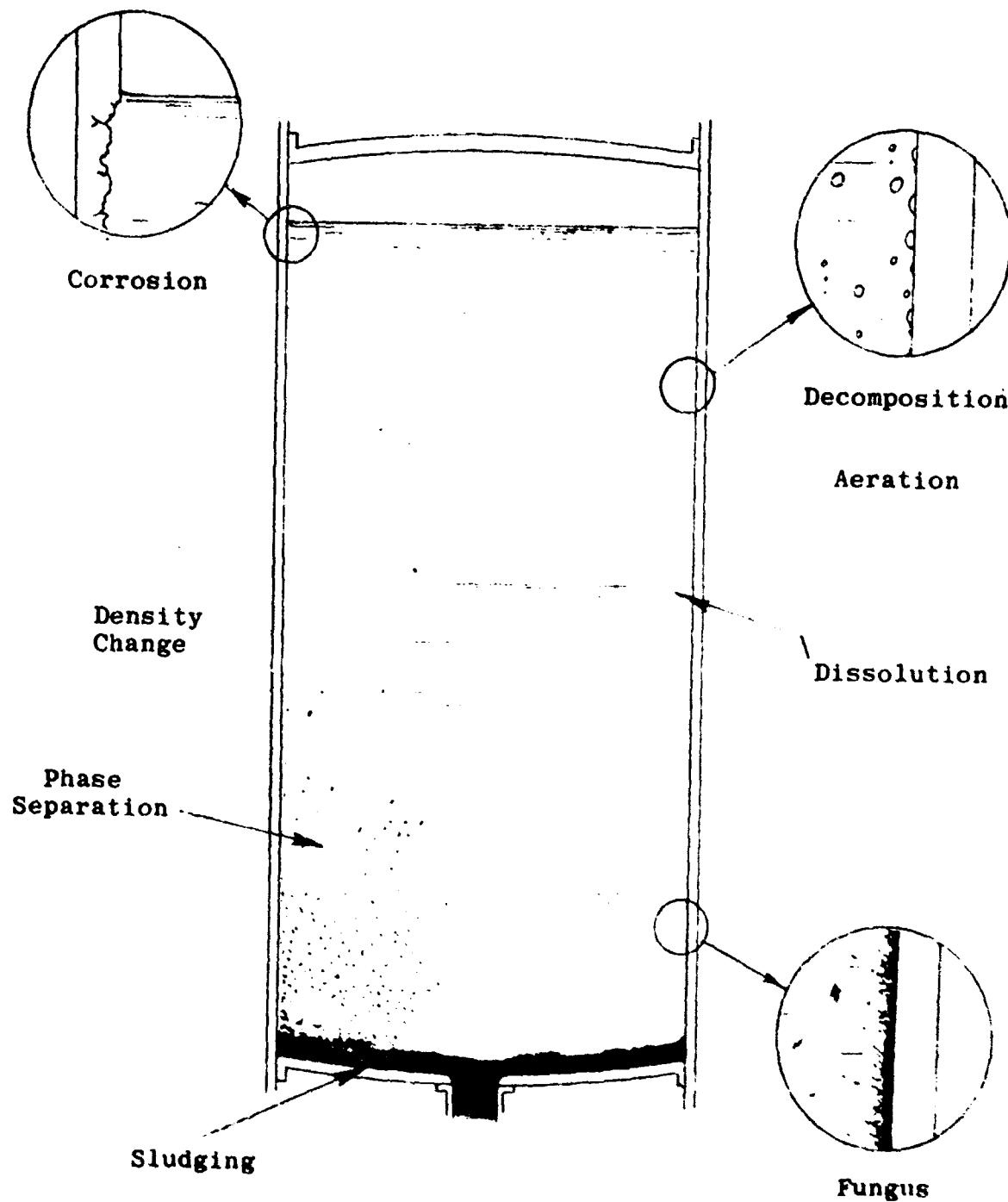


Figure 1. Potential Propellant Storage Effects

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TABLE II  
EFFECT OF PROPELLANT DEGRADATION

Propellant	Mode of Degradation					Physical Transformation
	Wall Reduction	Film Formation	Sludge Formation	Gas Generation	Gas Generation	
N <sub>2</sub> O <sub>4</sub>	2	2	2	2	3	3
H <sub>2</sub> O <sub>2</sub>	2	2	2	1	1	3
C <sub>TF</sub>	1	2	2	3	3	3
Oxidizers	2	2	2	3	3	3
Compound A	2	2	2	3	3	3
N <sub>2</sub> H <sub>4</sub>	3	3	3	2	1	3
NH <sub>4</sub> I	1	3	3	2	1	3
UDITH	1	3	1	2	1	3
Fuels	3	3	3	2	1	3
Verozine 50	3	3	3	2	1	3
NH <sub>4</sub> F-1	3	3	3	2	1	3
NH <sub>4</sub> F-5	3	3	3	1	1	3

## Legend:

- 1 - Severe
- 2 - Moderate
- 3 - Negligible

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Propellant degradation results in a reaction which changes the average molecular weight of the residual liquid and changes physical properties such as resistance, thermal conductance, optical density to specific wavelengths, and dipole moment.

#### B. Environmental Conditions

To effectively select and design an NDT device for any given application, the physical aspects of the end-item and the environmental conditions to be encountered must also be considered. The techniques studied in this program were to be applicable to air launch, silo launch, and mobile launch missiles, which each have their own unique requirements. The launch and operational conditions for the three launching modes are summarized in Table III (pg 11).

Air launched propulsion systems utilizing liquid propellants, which have been extensively used over the past several years, are typified by the Bullpup A and B systems. These units are of the packaged liquid powerplant type in which the propulsion system is a true "ordnance round" which is mass produced, hermetically sealed and requires zero maintenance. The reliability of this system has been extremely high and, as currently used, has little or no need for field monitoring. The design approach, however, is characteristic of future advanced air launched missiles using more energetic propellants. The sealed unit philosophy would dictate that the monitoring medium be one which is external to the unit and totally independent of it. Malfunction of the monitoring system cannot adversely affect function or performance of the propulsion system. Limitations of the monitoring system restricts the propellant effects which can be monitored and their relation to the overall reliability of the propulsion system.

If the NDT sensing device is considered an integral part of the propulsion system, it is evident that the component must possess the same or better aging and reliability properties as the system itself. The environmental requirements are formidable and include a five-year minimum shelf life, vibration and acceleration stability, a temperature range from -65°F to +175°F, and resistance to humidity, fungus, rain, salt spray, sand and dust.

Propellants used in a silo-launched vehicle (ICBM) are probably the easiest of the three launch conditions in which to monitor propellant condition. In this application, the propellants are stored in a fixed position with the temperature and humidity closely controlled. Since the missile is stored in a permanent position, NDT devices can be attached or positioned on a nominal full time basis. The obvious limitations are that monitoring the propellant at a given station will not necessarily be representative since there will be a minimum of convective circulation in a large tank at a constant temperature and a large number of detection points may be required. However, sludge will settle to predetermined locations at the bottom where it can be sensed readily. Because of general inaccessibility, monitoring will be remote and the leads must be permanently attached.

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TABLE III  
ANTICIPATED LAUNCH AND OPERATIONAL CONDITIONS

Launch Mode	Mobile	Silo	Air
Life	5 yr.	5 yr.	5 yr.
Usage (non-propulsion)	250 short distance moves	---	750 flight missions
Temperature Range	60 + 20 °F	65 + 5 °F	-65 to +175 °F
Humidity	25 + 5 %	25 + 5 %	10 - 100 %
Vibration	3 g's at 5 cps	---	1.4 g's at 35 cps

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For the mobile launch application, the degree of difficulty in applying NDT lies between the air launch and silo launch and is closest to the air launch case. Mobile missiles may be of the packaged liquid type, in which case the problems and limitations would be essentially similar to those of the air launched packaged units, except for less severe environments. If the system design were similar to silo-stored vehicles, the accessibility restraints would be minimized, but more severe vibration conditions would be imposed. The fact that the system is normally stored in a horizontal position and then erected vertically for use makes propellant orientation a variable. Therefore, additional sensors may be required to monitor both attitudes.

#### C. Detection Methods

The rationale of the detector study was based on achieving a maximum reliability and a minimum of interference with the missile operation. The methods must provide direct indications of the ability of the propulsion system to carry out its mission by meeting the following criteria. The chemical component or phenomena which is being measured must be directly related to the success or failure of the mission. The instrumentation chosen must have an intrinsic sensitivity and stability so that a go-no-go status may be anticipated and unequivocally determined. The choice of an actual device to be applied to the missile must be weighed inversely with regard to any limitations on the operational readiness.

The methods for monitoring propellants can be generally divided into two classifications, external and internal devices. The external types of instrumentation include those which do not contact the container walls and those which may be attached to the walls but do not enter the metal surface. The primary emphasis in this program was directed toward development of externally applied instruments. Because of the great degree of complexity involved in the chemical behavior of individual combinations of propellants and tankage, a phenomenological view was adopted in the consideration of NDT methods. This approach avoids the errors and unforeseen developments which accompany the sensing of individual chemical entities by specific means of chemical detection.

In the initial studies on non-destructive testing methods undertaken for this program, a wide variety of methods were considered. The seven most promising methods which include gamma absorption, neutron absorption, ultrasonics, pressure, capacitance, conductance, and optical absorption have been evaluated for their general applicability to propellant degradation in Table IV (pg 13). The same degradation modes or effects which were listed in Table II (pg 9) are retained in Table IV, but the seven detection methods under consideration were substituted for the listing of propellants. The same type of numerical rating system is used with (1) representing a good detector potential to (3) being a poor potential. By matching Tables II and IV, it is possible to quickly match a detector-effect combination for a specific propellant by comparing equivalent blocks. Any combination of (1)'s and (2)'s allows consideration of that detection method for that propellant.

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TABLE IV  
GENERAL APPLICABILITY OF DETECTION METHODS TO PROPELLANT DEGRADATION

Utility of Detection Method in General Applications	Mode of Degradation						Physical Transformation
	Wall Reduction	Wall Interaction	Film Formation	Sludge Formation	Gas Generation	Self Decomposition	
Gamma Absorption	1	3	2	3	2	2	Viscosity Change
Neutron Absorption	3	1	2	2	1	2	Phase Separation
Ultrasonics	1	2	1	2	2	1	2
Pressure	3	3	3	1	1	3	2
Capacitance	3	3	1	3	3	2	1
Conductance	3	3	1	3	1	3	1
Optical Absorption	3	3	2	3	2	3	3

## Legend

- 1 - Good potential
- 2 - Moderate potential
- 3 - Poor potential

NOTE: This table is used in conjunction with Table II (pg. 9 ) as explained on page 12 .

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The two propellants of primary interest for this program were Compound A and MHF-5. The potential detection methods for these two propellants are shown in Tables V and VI (pgs 15 and 16 respectively). The numerical values are based upon a combined weighting of the occurrence of a phenomenon and the ability of the instrumentation to monitor it. From this analysis one can observe that for the two propellants of principal interest, pressure monitoring of MHF-5 and corrosion/sludge formation for Compound A are the major considerations.

The four methods ultimately considered for Compound A and MHF-5 were ultrasonic testing, strain-gage pressure measurement, thermal conductivity measurement, and penetrating radiation. The first three methods were evaluated in the second phase of the program and the principle of the technique, details of operation, means of application, and their relative advantage and disadvantage with respect to competing methods will be given in subsequent sections of this report. The fourth technique, penetrating radiation, will be discussed here, but was not experimentally evaluated.

The penetrating radiation was considered for measuring wall thickness to detect gross corrosion and the resultant wall thinning. There are relatively few portable radiation devices which are commercially available and can give rapid, on-the-spot results. There are a number of radiographic systems which are quite reliable for weld analysis and some thickness measurements, but the sources (such as gammas from iridium 192) must be heavily shielded and the radiographs require a photo lab and qualified radiographers for proper development and interpretation. Shielding protection and strict governmental regulations must be complied with at all times.

Simpler devices operate by transmission or backscatter utilizing relatively weak gamma sources (such as 25 millicuries of AM-241) and a scintillation counter for detection. The only device which was portable and accurate that could be found in the literature was the Giannini Thickness Gage. It is fast, has a meter read-out, weighs only 9 pounds and is fairly safe. This device can be used with aluminum tanks, but it cannot measure 0.1 inch thick steel walls. The prospects for locating sludge and gas pockets have not been established and are not believed to be favorable. The radiation thickness gage costs about the same as the ultrasonic equipment which was evaluated on this program. Half life of the radiation sources exceed the five year requirement and maintenance should be minimal.

#### D. Selected Techniques

The analytical investigation of the non-destructive test methods applicable to the propellant degradation modes led to the selection of techniques which were used in the course of the remainder of the program.

1. The detection, measurement and monitoring of changes in wall thickness, sludge and gas pocket formation derived from corrosive propellants, primary oxidizers, should be accomplished with the pulse-echo ultrasonic testing methods.

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TABLE V  
APPLICABLE DETECTION TECHNIQUES FOR COMPOUND A

Utility of Detection Method in General Applications	Mode of Degradation				Physical Transformation				
	Wall Reduction	Wall Interation	Sludge Formation	Gas Generation	Gas Generation	Sludge Formation	Density Change	Phase Separation	Viscosity Change
Gamma Absorption	2		2						
Neutron Absorption			2						
Ultrasonics	1	2	1						
Pressure									
Capacitance			2						
Conductance				2					
Optical Absorption				2					

NOTE: Empty blocks correspond to ratings of 3 in Table II or IV and have a low potential.

## Legend

1 - Good potential

2 - Moderate potential

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TABLE VI  
APPLICABLE DETECTION TECHNIQUES FOR MHF-5

Utility of Detection Method in General Applications	Mode of Degradation						Physical Transformation		
	Wall Reduction	Film Formation	Sludge Formation	Gas Generation	Gas Formation	Sludge Change	Density Change	Phase Separation	Viscosity Change
Gamma Absorption					2			2	
Neutron Absorption				2	2			2	
Ultrasonics				2	2			2	
Pressure				1	1				
Capacitance							2		
Conductance									
Optical Absorption						2			

## Legend

NOTE: Empty blocks correspond to ratings of 3 in Table II or IV and have a low potential.

1 - Good potential

2 - Moderate potential

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2. A secondary approach to measuring these effects is the use of penetrating radiation by transmission and back-scattering. Thus far, this method is limited to aluminum materials and its efficiency for detecting sludge and gas formation has not been determined, but it is doubtful. This method should be evaluated only if the ultrasonic technique is inadequate.

3. Strain-gage instrumentation is well established and is uniquely applicable for the measurement of pressure build-up due to propellant gaseous formation, primarily from hydrazine-based fuels.

4. A thermal conductivity probe can detect propellant leakage as a result of variation of thermal conductivity in the storage environment. Proper placement of measuring devices at potential leakage or tank malfunction points will permit monitoring of this degradation mode. Changes can be measured by thermal conductivity cells composed of a basic Wheatstone bridge coupled to suitable indicating or controlling units.

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## IV

## PHASE II, TASK 1, EXPERIMENTAL INVESTIGATION

Evaluation tests were conducted with the three chosen NDT techniques to optimize their application to the propellant degradation effects. These tests used actual tank materials of construction and scaled dimensions. The ultrasonic and strain gage tests used water for a simulated liquid propellant to eliminate hazardous conditions in these preliminary tests. The thermal conductivity tests were made with Compound A and MHF-5.

**A. Ultrasonic Testing**

Of the several available means for ultrasonic testing, the pulse-echo method was most appropriate for the requirements of this program since the literature survey indicated potential capabilities beyond simple thickness measurements. Several manufacturers make commercially available equipment which is suitable for the evaluation tests.

**1. Principle of Operation**

Sound travels by small elastic displacements of a medium. When a short burst of sound passes perpendicularly through a smooth surface separating two materials, several processes may occur, depending on the difference in acoustic impedances of the media. This impedance depends upon the density of the material and the velocity of sound in it. When the impedances are similar, much of the sound energy is transmitted through the boundary. However, if the impedances differ (such as found at solid/liquid, solid/gas, and liquid/gas interfaces) a sizeable proportion of the energy is reflected toward the source. The intensity of the returned energy and its travel time are related to the nature of the boundary, the thickness of the material layers and the velocity of sound in the specific substance.

An ultrasonic system for pulse-echo measurements is shown in Figure 2 (pg 20). The pulse-echo measurements are made by generating an electrical pulse in the requisite frequency range in the instrument. This pulse is transmitted to a transducer or search unit which converts the electrical energy to ultrasonic (mechanical) vibrations. The high frequency sound pulse is transmitted from the transducer into the test specimen. The pulse is reflected from a boundary, such as a flaw or the far side of the specimen, and returns to the transducer where it is converted back to electrical energy. The signals are amplified and presented on a cathode-ray tube screen with the sweep synchronized to the original pulse. The horizontal position and amplitude of the vertical pips indicate the nature of the reflecting surface. The three signals in Figure 2 represent the original pulse on the left, the flaw in the center and the back surface of the test specimen on the right of the CRT screen.

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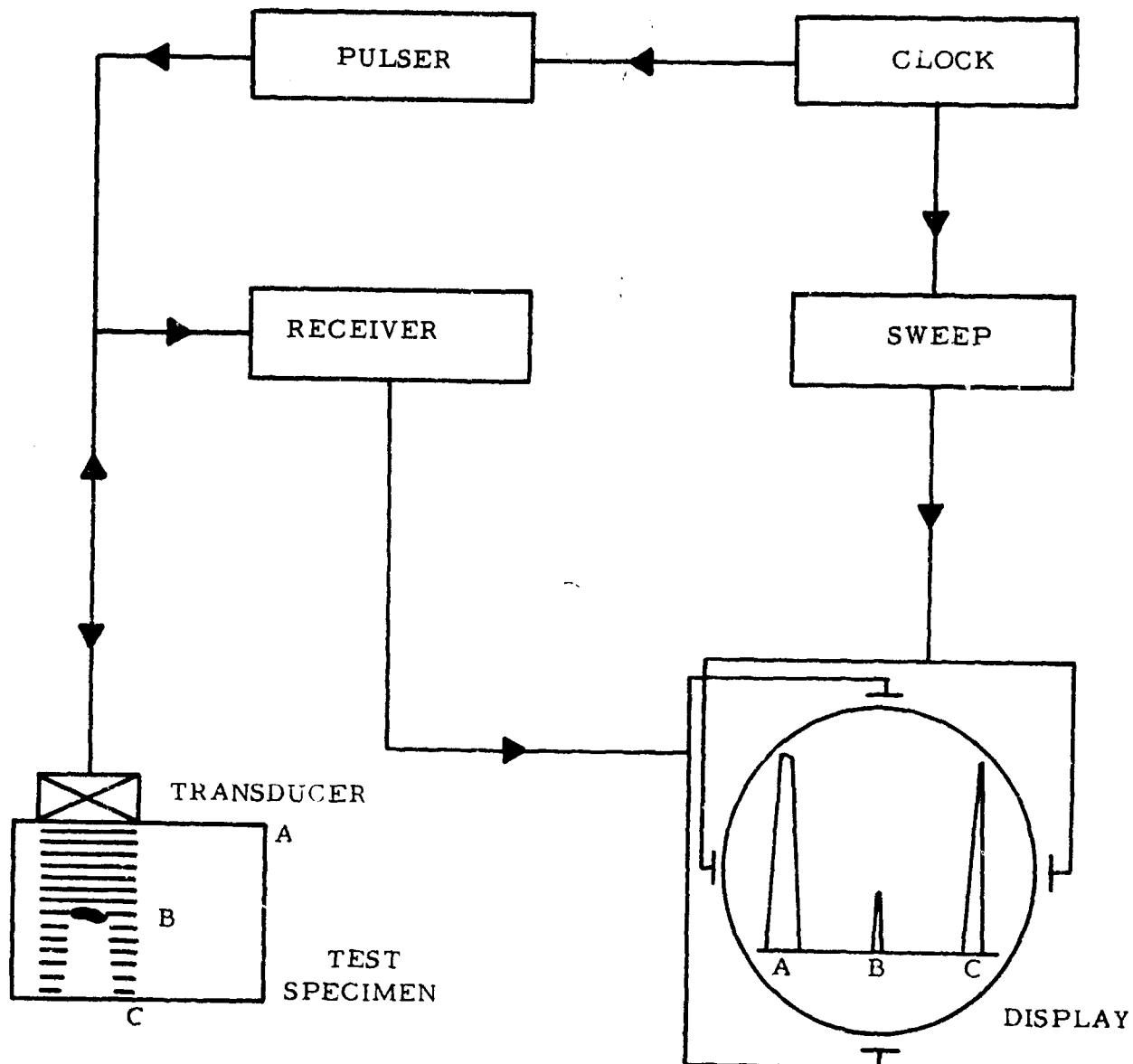
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Figure 2. Block Diagram of Pulse Echo Equipment

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## 2. Equipment

The ultrasonic test equipment chosen for evaluation in this program was the Sonoray, Model 301, Ultrasonic Flaw-Thickness Tester manufactured by Branson Instruments, Inc. The Sonoray is a portable, battery-operated instrument operating on the pulse-echo principle. The unit is specifically constructed for rugged field use and is currently widely used in industry. The Sonoray and auxiliary equipment are shown in Figure 3 (pg 22) with the Sonoray on the right. The battery charger, in the center of the photograph, permits operation of the Sonoray on 110 VAC in the lab and recharges the Nicad batteries which are contained in the Sonoray case. The Digital Micrometer, on the left, provides numerical readout of thickness to three digits. The transducer attached to the Sonoray is a dual element model with separate transmitter and receiver elements.

The four ultrasonic transducers used in this program are shown in Figure 4 (pg 23). The thin crystal of piezoelectric material that reversibly converts high frequency electrical energy into high frequency sound waves is a ceramic for these transducers. The frequency is 5.0 MHz with a pulse repetition rate of 1.0 KHz generated by the Sonoray.

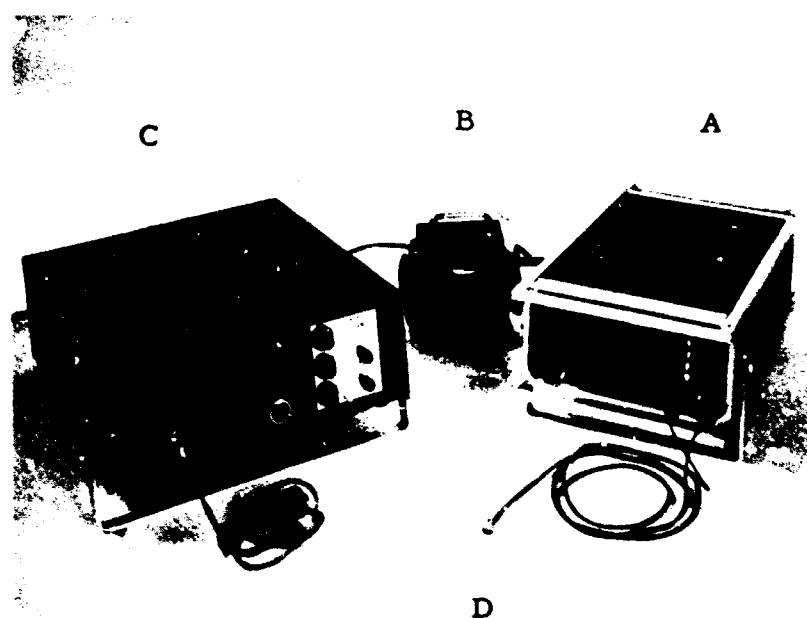
The transducer at the right side of Figure 4 is a 1/2 inch dual element transducer with transmitter and receiver elements separated by an insulator. A plastic delayline in the receiver circuit provides more separation between the transmitted pulse and the reflected signal to measure thin materials or detect flaws near (to within 0.050 inch) the front surface of the material. The transmitter and receiver elements are angled slightly which introduces a non-linearity in measuring very thin materials as will be discussed in a later section.

The transducer over the right end of the ruler is a 1/4 inch single element transducer. The same ceramic crystal is used to transmit the pulse and receive the echo. It is difficult to measure material thicknesses below about 0.2 inch in aluminum with the single element due to overlap of the transmitted and reflected signals on the Sonoray. A larger, 3/4 inch, single element transducer is shown at the left end of the ruler. A rubber membrane attached by an end cap enables tests to be made on rough surfaces.

The fourth transducer is for angle beam testing. The transducer has a 1/2 x 1/2 inch active area and is mounted on a plastic wedge. The angle in the plastic between the transducer mounting surface and the work piece surface determines the mode conversion of the ultrasonic waves. The sound waves will bounce between the parallel surfaces in a thin piece until a flaw is detected or the energy is dissipated. If the angle increases, surface waves will be generated which will not penetrate into the work piece, but will travel along the near surface.

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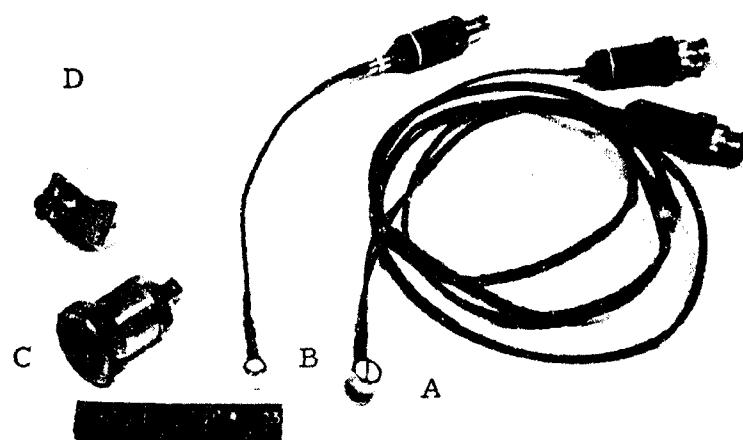
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Figure 3. Ultrasonic Test Equipment - (A) Sonoray,  
(B) Battery Charger, (C) Digital Micrometer  
and (D) Dual-Element Transducer

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Figure 4. Ultrasonic Transducers - (A) Dual Element,  
(B) 1/4-in. Single Element, (C) 3/4-in.  
Single Element, (D) Angle Beam



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Figure 5. Calibration Standards

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### 3. Test Items

Test items of various materials and configurations were fabricated to define the capabilities and possible limitations of the ultrasonic techniques.

Samples of representative materials, including 1100-0, 2014-T3, 2024-T351, 6061-T6, 7075-T6 aluminums and 304, 316, 321 and 347 stainless steels, were obtained. The samples were machined to a standard size of 2.0 inch diameter and 0.100 inch in thickness.

Step blocks of steel, with steps from 0.500 to 0.100 inch which were furnished with the ultrasonic equipment, are shown in Figure 5 (pg 23). Another set of blocks was made of 2024-T4 aluminum alloy with an additional 0.050 inch step. Finer depth graduations were needed for the thinner materials since the calibration is not linear in this range; therefore a series of 12 flat-bottomed one-inch holes were drilled in a 2024 aluminum plate with wall thicknesses of 0.129 to 0.013 inch. This plate is also shown in Figure 5. A similar plate with one-inch holes was made from 316 stainless steel. These blocks and plates were measured with mechanical micrometers and were used primarily as reference standards for calibrating the ultrasonic equipment.

The 1/4 inch flat aluminum plate shown in Figure 6 (pg 25) was drilled with 1/16 inch to one-inch diameter flat bottom drills to produce wall thicknesses from 0.250 to 0.050 inch. The same hole pattern was duplicated to another 1/4-inch plate and rolled into a 10-inch diameter tank 9 inches high, seam welded, and a plate welded on one end as shown in Figure 7 (pg 25). Also shown in the foreground of this figure is a smaller tank fabricated from 2-3/4 inch OD x 1/8 inch thick wall 2024 tubing. Several of these were made and the particular one shown here had three slots milled the length of the tube to produce local wall thicknesses of 0.050, 0.075, and 0.100 inch. The inside of the tank then was corroded with a 37 percent HCl solution to a 150 rms surface finish to simulate propellant corrosion. The third tank in this figure is drawn from 1100 aluminum and is 3.0 inches in diameter with an 0.020 inch wall.

A second 10-inch diameter tank was also made from the 1/4 inch aluminum plate. Six 1/2 inch wide slots were milled in this tank to produce wall thicknesses from 0.25 to 0.050 inch and the inside was corroded with the 37 percent HCl solution.

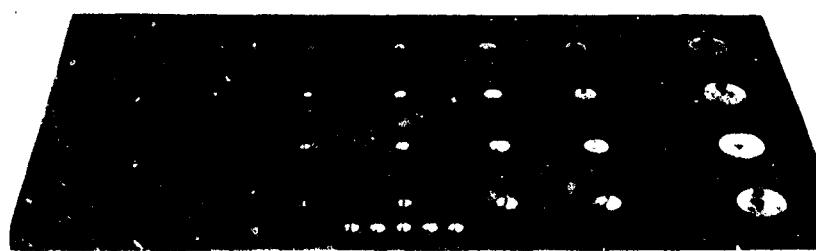
### 4. Test Results

The preceding test items were used to evaluate 16 test variables which included type of material, thickness, flaws, curvature, roughness, couplant, transducer orientation, transducer type, corrosion, interface, bubbles, sludge, liquid, liners, coatings, and foreign material. The individual variables will be discussed in more detail and the results of the tests will be explained in this section.

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Figure 6. Test Piece for Simulated Flaws



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Figure 7. Test Tanks

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**UNCLASSIFIED****a. Material**

Each type of material has a characteristic velocity of sound associated with it. Even in a single class of material, such as aluminum, the velocity depends on the particular alloy and even the temper of the material. The Sonoray was calibrated for 2024 aluminum and the thickness of the 2-inch discs of the various aluminums was measured. All the alloys measured within 0.001 inch of the true thickness. For the thin material thicknesses and the accuracy of the Sonoray equipment, there are no discernable differences between the aluminum alloys tested. Similarly, all the four stainless steel samples appeared the same when the instrumentation was recalibrated for the difference in sound velocity between aluminum and steel.

**b. Thickness**

To measure the thickness of a piece of material, the Sonoray and digital micrometer were calibrated with the standard blocks which have been shown in Figure 5 (pg 23). The single element transducers can measure thicknesses down to about 0.20 inch and are limited by the ability to separate the leading edge of the echo from the preceeding signal as the two signals get closer together on the Sonoray scope face. For measurements below 0.5 inch, the dual element transducer is recommended because the delay line separates the echo from the transmitted signal. Table VII (pg 27) shows two sets of measurements taken with the 1/2 inch dual element transducer using 2024 aluminum standards. The first six readings in each column are from the standard blocks and the other twelve readings are from the plate with the 1 inch flat-bottom holes. If the ultrasonic equipment is calibrated at 0.5 and 0.2 inch, as in the first measured column of Table VII, thicknesses below 0.2 inch will indicate higher than the true value. This is because the two crystals in the dual element transducer are angled toward each other and a noticeable non-linearity develops in thin material. Below 0.040 to 0.050 inch, the electronics of the Sonoray cannot recover quickly enough to accept the echo and an erroneously high reading develops. Even though the indicated thicknesses are not true from 0.200 to 0.050 inch, the readings are reproducible and a repeatable calibration could be developed. The last column in Table VII shows that thinner materials can be read accurately if thinner calibration standards are used. Therefore, if the general range of the wall is known in advance, the Sonoray can be calibrated to read the true thickness within 0.001 inch. The calibration will last for at least several hours of operation of the Sonoray equipment before it begins to drift. Similar results were obtained with the stainless steel plate within the 1 inch flat-bottom holes.

**c. Flaws**

The flat-bottom holes in the plate in Figure 6 (pg 25) and the tank in Figure 7 (pg 25) were used to determine the effect of flaw size and depth on the accuracy of detection. Table VIII (pg 28) summarizes a set of

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TABLE VII  
MATERIAL THICKNESS OF 2024 ALUMINUM PLATE

True Thickness (in.)	Measured Thickness (in.)	
	A*	B**
0.500	0.500	0.562
0.400	0.400	0.444
0.298	0.297	0.325
0.200	0.200	0.210
0.100	0.103	0.100
0.050	0.060	0.050
0.129	0.131	0.129
0.118	0.122	0.118
0.109	0.112	0.108
0.097	0.100	0.096
0.087	0.094	0.087
0.078	0.087	0.078
0.075	0.084	0.076
0.067	0.077	0.068
0.053	0.063	0.053
0.044	0.058	0.047
0.029	0.126	0.124
0.013	0.115	0.108

\* Transducer (dual element) calibrated between 0.200 in. and 0.500 in.

\*\* Transducer (dual element) calibrated between 0.053 in. and 0.129 in.

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TABLE VIII  
MEASUREMENT OF FLAWS

Hole Dia., (in.)	Flat Plate Thickness		10-in. Tank Thickness	
	True (in.)	Meas. (in.)	True (in.)	Meas. (in.)
1	0.250	0.250*	0.250	0.250
1/2	0.250	0.249	0.250	0.250
3/8	0.250	0.247	0.248	0.246
1/4	0.253	0.250	0.254	0.254
3/16	0.253	0.251	0.251	0.250
1/8	0.254	0.257	0.251	0.252
1/16	0.254	0.262	0.250	0.263
1	0.209	0.209	0.206	0.206
1/2	0.211	0.209	0.208	0.206
3/8	0.209	0.204	0.204	0.205
1/4	0.211	0.207	0.211	0.210
3/16	0.213	0.210	0.204	0.207
1/8	0.215	0.210	0.208	0.212
1/16	0.210	0.222	0.209	0.248
1	0.109	0.109*	0.108	0.108
1/2	0.111	0.108	0.106	0.106
3/8	0.109	0.105	0.107	0.106
1/4	0.117	0.116	0.113	0.113
3/16	0.112	0.109	0.107	0.110
1/8	0.112	0.114	0.110	0.110
1/16	0.109	0.122	0.107	0.117
1	0.050	0.052	0.054	0.064
1/2	0.050	0.052	0.045	0.052
3/8	0.050	0.050	0.045	0.053
1/4	0.050	0.050	0.053	0.057
3/16	0.047	0.050	0.047	0.054
1/8	0.046	0.050	0.059	0.056
1/16	0.049	0.056	0.053	0.062

\* Calibration points  
Dual element transducer

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data taken on both the flat plate and the tank. When used on a curved surface, such as the tank, the dual transducer must be positioned with the divider on the face of the transducer at right angles to the tank axis and the transducer is rocked back and forth to obtain the minimum reading. The 1/16 inch sample holes are difficult to find with this size transducer and indicate a thicker material than the true value. This may be caused by a reflection from the side rather than the bottom end of the drilled hole. Available smaller diameter dual transducers would be capable of accurately measuring the smaller diameter holes.

The angle beam transducer and plastic wedge were also used to detect the flaws. This transducer can locate the presence of small defects, such as the 1/16 inch holes, but does not measure the size of the defects. A dual element transducer must be used for size determination.

d. Curvature

Thickness measurements and flaw detection were made on the flat plates, 10-inch diameter tanks and 2-3/4 inch diameter tanks. The flat-face transducers could produce accurate readings over this curvature range if the elements were oriented correctly and the transducer was slowly rocked back and forth to find the minimum value. For a specific tank application, a special transducer with a curved surface could be fabricated.

e. Roughness

Roughened areas were made on a flat plate and inside the ten-inch diameter tank. A series of V-groove slots were milled parallel to each other. In the three groups of grooves, the grooves were spaced 0.050 inch apart and the depth from the surface to the bottom of the vee was 0.005, 0.010, and 0.050 inch respectively. Thickness measurements taken from the opposite side of the plate or tank wall measured the minimum wall thickness to the bottom of the groove. On an irregular surface, the ultrasonic transducer will measure the minimum wall thickness providing the minimum is not too small to be detected as was demonstrated by the flaw tests. The surface to which the transducer is applied must be smooth enough to form an adequate coupling between the transducer and the piece which is being measured.

f. Couplant

The couplant between the transducer and work piece is very important to the operation of an ultrasonic system because the thin air film between the transducer and the work surface is sufficient to prevent the sound wave from entering into and returning from the work piece. The desirable properties of a suitable couplant are that it wet the surface of the transducer and the test material to exclude all air between them. It must be easily applied and must not run off the surface too fast, particularly for vertical surfaces. The couplant should be homogeneous, free from any

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bubbles or solid particles, and should not be corrosive or toxic. An ideal couplant would have the same acoustic impedance as the test material, but this can rarely be realized in practice.

Water is commonly used for a couplant, but its chief drawback is its low viscosity. The majority of the measurements in this program were made with a glycerin couplant which is satisfactory at room temperatures, but which freezes at 62F. An oil or grease such as Dow Corning 33 grease with a -100F to +350F range would be suitable for the -65F requirements of this program. This grease was satisfactory in room temperature tests.

Solid materials can also be used as couplants. The rubber diaphragm of the 3/4 inch transducer had a film of oil between the transducer and the inside of the cap, but the outside surface was dry. Without any external liquid couplant, the echo signal was about half the amplitude of that obtained with liquid couplant. For the applications of this program, the Sonoray gain was sufficient to compensate for this signal attenuation.

g. Corrosion

The 10-inch diameter tank with the milled slots, two 2-3/4 inch diameter tanks, and five 2 x 2 inch aluminum plates were corroded with 37 percent concentrated HC1. Since the acid produced a fairly smooth surface etching, the finish was measured with a Profilometer (Micrometrical Manufacturing Co.) to determine the rms value. The original aluminum surface was 20 rms and the corrosion varied from 100 to 250 rms. One side of each 2 x 2 inch sample was machined to provide a smooth surface on which to apply the transducer. With a smooth back surface, as on the original aluminum with the 20 rms finish, the ultrasonic signal is readily reflected between the two surfaces many times with little loss in signal amplitude after multiple reflections. As the surface roughens, the reflections become scattered and the signal amplitude is attenuated in proportion to the surface roughness. The amplitude is quite sensitive to the degree of corrosion. For example, the gain control on the Sonoray can be set to show half screen deflection for a 130-rms surface, no deflection for 250 rms, and over full screen deflection for the 20 rms surface. By comparing the relative deflection from an unknown sample with the standards, the degree of corrosion on the far side of a sample piece can be determined. This was done in the ullage portion of the tanks as well as with the flat sample.

With the liquid behind the tank wall, some of the ultrasonic energy is transmitted into the liquid and the reflections are decreased in number and amplitude. It is still possible to detect the corroded surfaces, but the sensitivity is decreased by about a factor of four. It was just possible to differentiate between the 150 rms inner surface and an uncorroded surface in two of the 2-3/4 inch tanks.

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**UNCLASSIFIED**h. Interface

The interface between the liquid and vapor phases in a tank can be detected by traversing up the outside vertical surface of the tank or by measuring the distance to the top of the liquid from the bottom of the tank. The second method requires calibration of the ultrasonic equipment for the particular liquid contained in the tank since the sonic velocity changes for various liquids.

If the transducer is placed on the vertical surface of a tank below the liquid surface level, the Sonoray controls can be adjusted to receive a signal transmitted through the liquid and reflected from the opposite tank wall. By traversing the tank wall vertically until this echo disappears, the liquid interface can be found. Using the 1/4 inch single element transducer, the surface level can be determined within 1/16 inch. Also, above the liquid surface, the ultrasonic signal can reflect between the tank wall surfaces more times since no energy is dissipated into the liquid. The increased number of reflections is also an indication of the interface location.

For the alternate method of liquid level determination, the transducer is placed at the bottom of the tank and the controls set to receive the reflected signal from the liquid-air interface. If the initial level is known, the change in level can be measured by the location of the reflected signal on the Sonoray screen. This method can follow a changing level, but requires a calibration.

i. Bubbles

Decomposition of propellants can produce high gas evolution rates. Gas bubbles were simulated by a stream of air bubbles released at the bottom of the tank. The ultrasonic system was set up to monitor the signal reflected from the far tank wall and any bubble passing through the ultrasonic beam momentarily interrupted the return signal. The signal interruption was detected on the Sonoray by a loss of signal which appeared to be a flicker. The rate of flicker indicates the frequency, but not the size, of the gas bubble evolution. If gas is trapped on the inside wall of the tank, the signal will be reflected at the local points of entrapment if the tank is scanned on the outside with a transducer.

j. Sludge

If a propellant degrades during storage, a sludge may collect at the bottom of the tank, particularly if there is a reaction between the propellant and the tank wall. Different types of sludges were simulated with aluminum flakes, 200 mesh  $\text{Al}_2\text{O}_3$  powder, and a mixture of carborundum and steel particles from a grinding wheel. The aluminum flakes were easily detected when scattered on the bottom of the tank by observing the attenuation of the signal reflected from the liquid surface of the tank. The other two

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finer materials transmit the ultrasonic beam more readily and about a 1/16 inch layer is needed for a positive identification of signal attenuation. A higher frequency transducer might be more sensitive to a thinner layer of sludge, but all the transducers used to date have been 5.0 MHz. If the 200 mesh Al<sub>2</sub>O<sub>3</sub> is stirred vigorously, it will take several minutes to settle out. The suspended solids can be seen by a signal attenuation from the far wall reflection looking through the side wall of the tank. This is due to partial signal scatter from the individual particles of Al<sub>2</sub>O<sub>3</sub>.

k. Liquid

The only liquid used in the tanks in these evaluation tests was water. Additional experience was gained with actual propellants during the last three months of the program. Theoretically, it should be possible to differentiate between different types of liquid in a closed tank due to their different acoustic velocities.

l. Coatings

Sample aluminum plates (Type 2024) and a small tank were cleaned and painted per the specifications for the LR 62-RM-4 (Bullpup) packaged liquid rocket engine. Some areas had the zinc chromate primer only while other had the primer plus two coats of lacquer. The paint attenuates the signals, but the instrument gain was sufficient to permit measuring wall thickness, locating liquid levels, etc.

m. Foreign Materials

The pulse echo ultrasonic equipment can also be used to detect foreign materials in a tank of propellant using either the single or dual element transducer. Typical materials used in the study were sponges, O-rings, metal objects, slivers of wood, and single blades of grass. If the object has a rough surface, such as the sponge, or if one surface is perpendicular to the ultrasonic beam, the energy will be reflected back to the transducer. Location within the tank can be determined and the general shape of the object defined by surveying it from several positions around the tank. The thinner tank walls (0.020 inch) were better for this technique because less internal reflections were generated in the wall. The multiple reflections can cause an object that is very close to the near wall to become lost in the clutter on the initial end of the scope display.

Another technique for locating the foreign objects is to look for the far tank wall. Any intervening object will block the wall reflection even if it does not generate a detectable signal of its own. The outline of the object can be defined by this method, but the distance from the tank wall cannot be determined. Another variation is to use through transmission where the transmitter and receiver transducer are separate and are located on opposite sides of the tank. Any foreign object will interrupt the signal between the transducers. All these techniques were tried successfully on the various

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size objects. The larger the transducer, the more rapidly the tank can be scanned, but the larger the object must be to intercept a significant portion of the ultrasonic energy.

### 5. Capabilities

As a result of these evaluation tests, it was concluded that this type of ultrasonic equipment would be satisfactory for monitoring the long-term storage of a corrosive propellant such as Compound A. It is recognized that the existing equipment is a general purpose instrument which is more complex than required for a specific application, but the ultrasonic principal can be used to develop a simple go-no-go type of monitoring gage. Specific performance and limitations of the equipment tested are as follows:

- a. Propellant corrosion can be detected in both the liquid and ullage portions of tanks. The degree of attack can be estimated by comparison with known samples corroded by the same medium.
- b. Propellant attack which results in reduction of the tank wall thickness can be monitored down to 0.050 inch with the current transducers.
- c. The liquid-vapor interface level can be monitored.
- d. Sludge buildup, foreign materials and bubbles can be detected inside a tank of propellant.

### B. Strain Gage Pressure Measurements

The major degradation effect of MHF-5 is gas generation. Therefore, one limiting characteristic of the propellant is the maximum pressure permissible in a given propellant tank. The buildup of gas within the system to a value which approaches this limit would be a good basis for rejection of the missile. This effect can be monitored by means of an external, bonded strain gage. Various types of strain gages, adhesives, and waterproofing techniques have been evaluated in this phase of the program.

#### 1. Principle of Operation

The resistance strain gage is a device which undergoes a change in resistance as its length varies. It is usually composed of fine metallic wire or foil and is bonded to a plastic coupon whose dimensions are much larger than the metal cross-section. This allows the bonding cement to transmit the strains from the test substance to the conductor. The strain sensitive element can also be a semiconductor material which changes resistivity much more rapidly making a more sensitive indicator.

The internal pressure,  $P$ , in a cylindrical tank is related to the hoop strain,  $\gamma$ , by the following expression:

$$P = -\frac{2 \gamma Y (R_o - 1)}{(R_o + 1)}$$

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where  $Y$  is Young's modulus of the tank material and  $R_o$  is the ratio of the outside to inside wall diameters. Since Young's modulus and the tank diameters are known or may be obtained, this equation allows the strain measurement to be converted to pressure within the range of elastic behavior of the tank wall.

The most commonly used electric circuit for obtaining strain measurements is some modification of the Wheatstone bridge. It permits signals from strain gages to be read individually, or to be combined with other gages which offers limitless computer and control possibilities.

## 2. Equipment

The strain gage test instrument was the Model P-350 Portable Digital Strain Indicator manufactured by the Budd Company, Instruments Division, of Phoenixville, Pa. This indicator, which is shown in Figure 8 (pg 35), is adaptable for quarter, half, and full bridge and has internal 120 and 350 ohm dummies. The gage factor is continuously adjustable from 0.10 to 10.00 and is calibrated from 1.50 to 4.50. The total reading range is  $\pm 50,000$  microinch/inch with an accuracy of  $\pm 0.1$  percent of the reading or 5 microinch/inch, whichever is greater, and a readability of 1 microinch/inch. A ten-turn potentiometer in the balance circuit has a dial to permit resetting the zero for subsequent readings. Power is furnished by a 9-volt battery and the weight is 7 pounds. The optional AC power supply was not purchased since the equipment was intended for field use.

The SB-1 Portable 10-Channel Switch and Balance Unit, also manufactured by Budd, was used with the Strain Indicator. Both units are shown in Figure 8. Up to 10 strain gages can be connected to gold-plated push clamp binding posts. A selector switch and individual ten-turn potentiometers permit rapid switching to read out multiple gage installations on the Strain Indicator. The Switch and Balance Unit is passive and does not require any power.

Four types of gages were evaluated including a foil strain gage, a foil temperature sensor, a wire strain gage, and a semiconductor strain gage. All the gages could be read out on the P-350 Strain Indicator.

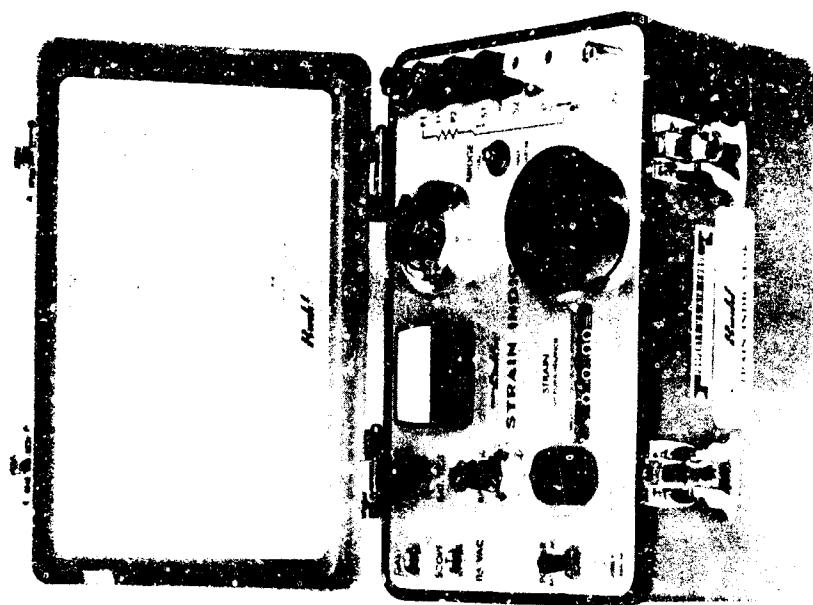
The metal film strain gages were purchased from Budd under their part numbers C12-144B-350 and C12-124A-350. The C12 indicates temperature compensation for aluminum and the 350 is the gage resistance in ohms. The middle digit of the center number is the nominal gage length in sixteenths of an inch and the other digits indicate constantan alloy material with epoxy fiberglass backing.

The S44-50 temperature sensor, also from Budd, is similar in appearance to a foil strain gage and can be used with the strain indicator to read temperatures from -100 to +600°F with an accuracy of  $\pm 1$  percent.

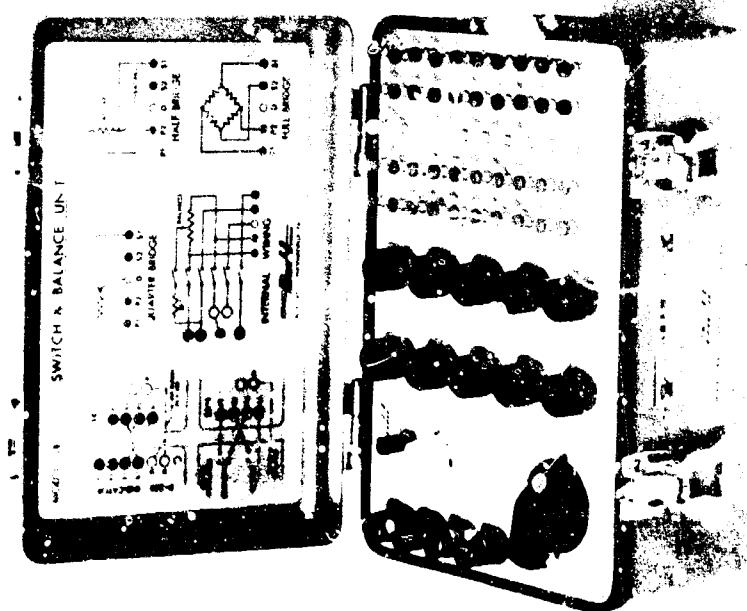
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(A)



(B)

Figure 8. (A) Strain Indicator and (B) Switch and Balance Unit

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When the MNT-120 linearizing resistor network is added, a change of 1F registers a reading of 100 microinch/inch on the strain indicator and the reading accuracy can be increased to  $\pm 0.1$ F. The sensors are mounted on the specimen surface by the same techniques as the foil strain gages.

The free-filament wire grid gages, type HT-435-8A-S13, were made by BLH Electronics, a division of Baldwin-Lima-Hamilton Corporation. These gages are specifically designed for flame spray installation, although they may also be applied with more conventional ceramic cements. In the Norton Rokide process, the surface is grit blasted with aluminum oxide and precoated with two or three mils of flame-sprayed alumina. The gage is placed on the precoated area and completely encapsulated with additional coatings of alumina. Gage clamping and elevated temperature cures are eliminated and the maximum metal temperature is less than 200F during the spraying. The specific gages used in the project were 1/2 inch long and were temperature compensated for aluminum.

The semiconductor gages are Type M(12)D-GP-350-500 dual element, temperature compensated gages manufactured by Kulite Semiconductor Products, Inc. The MP series gages are corrected for apparent strain on specific materials by matching a positive and a negative gage factor crystal in a single gage to provide two active temperature compensated arms with a composite gage factor in excess of 200. This compares to gage factors between two and four for metal wire and foil gages. The gage factor has a temperature coefficient of -14%/100F, for the 1/4 inch long gages used.

### 3. Test Items

Six tanks were fabricated from 2024 aluminum for the strain gage evaluation tests. Three tanks were 3.0 inch diameter with 0.120 inch walls, and the other three tanks were 4.0 inch diameter with 0.065 inch walls. All tanks were made from a 9 inch length of tubing with 1/4 inch thick flat end caps welded on each end. A 1/4 inch AN fitting was welded on one end for loading liquid and monitoring pressure. Except for length, these tanks were similar to Figure 18 (pg 62).

The six tanks were gaged with the four types of gages using various adhesives and waterproofing compounds as shown in Table IX (pg 37). The GA-2 is a two-part epoxy usable from -100F to +200F which requires a six-hour cure at 75F and 10 psi pressure. The GA-61 is also a two-part epoxy usable from -100F to +600F which requires a 2 hour cure at +200F and 10 psi pressure. The GW-2 waterproofing compound is a nitrile rubber which cures in less than 30 minutes at 75F, but cannot be immersed in water. The GW-5 two-part epoxy takes 6 hours to cure at 75F, but is good for water immersion at temperatures up to 180F.

The strain gages were equally spaced around the center of the tank and oriented to measure the hoop stress in the tank due to internal pressure. Temperature sensors were mounted both parallel to the tank

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**TABLE IX**  
**STRAIN GAGE APPLICATION SCHEDULE**

TANK			GAGE			Adhesive	Waterproofing GW-
No.	Dia. in.	Wall in.	No.	Length in.	Type		
1	3.0	0.12	1	1/4	foil	GA-2	5
2	4.0	0.065	2	1/4	foil	GA-2	2
			3	1/8	foil	GA-2	5
			4	1/8	foil	GA-2	2
			5	5/16	temp	GA-2	5
3	3.0	0.12	1	1/8	foil	GA-61	5
4	4.0	0.065	2	1/8	foil	GA-61	2
			3	1/4	foil	GA-61	5
			4	1/4	foil	GA-61	2
			5	5/16	temp	GA-61	2
5	3.0	0.12	1	1/2	wire	Rokide	5
6	4.0	0.065	2	1/2	wire	Rokide	2
			3	5/16	temp	GA-61	2
4	4.0	0.065	6	1/4	Semi-conductor	GA-61	2
5	3.0	0.12	4	1/4		GA-61	2

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axis to minimize the stress they encountered and perpendicular to the tank axis to determine the maximum apparent error due to internal pressure. The strain gages were wired for three-wire quarter-bridge circuits to minimize false strain readings due to ambient temperature changes on the lead wires. Either the internal 350 ohm dummy in the strain indicator or another strain gage on an unpressurized tank was used to make a half-bridge circuit for the foil and wire gages. The semiconductor gages with four leads were used as a half-bridge.

#### 4. Test Results

The various combinations of tanks, gages, adhesives, and waterproofing compounds were evaluated by pressure and temperature calibrations. The tanks were filled with water and pressurized with nitrogen to determine the linearity and repeatability of the strain gages as compared to a precision bourdon tube gage. The tanks were also placed in a temperature conditioning box and the apparent strain due to temperature measured between -65F and +175F. In addition, the zero balance was monitored to determine the stability over a two month period.

##### a. Metal Film Gages

The metal film strain gages are nominally temperature compensated for the thermal effects of the aluminum tank material. Even with this compensation, the manufacturer's specified nominal apparent strain is significant as shown by:

Temperature, F	-100	0	75	175
Apparent Strain, microin. /in.	$-650 \pm 100$	$-100 \pm 40$	0	$-50 \pm 20$

The actual apparent strain for a 1/4 inch foil gage is shown in the lower curve of Figure 9 (pg. 39). This is the apparent strain due to temperature, at 1 atmosphere pressure, for gage 2 on tank 1 when using the internal dummy in the strain indicator to form a half bridge. When the internal dummy is replaced with gage 1 on tank 1, which experiences the same temperature changes as gage 2, the apparent strain is indicated on the middle curve of Figure 9. The apparent strain is reduced to between +14 and -8 microin. /in. over the temperature range from -71F to +172F. These curves are typical for the 1/4 inch foil gages on tanks 1 and 2. The 1/8 inch gages were similar except for the curve with the temperature compensating dummy, which went as high as +40 microin. /in. at +172F and -140 microin. /in. at -71F. The larger fluctuations may be due to the smaller gage per se or to a mismatch between the characteristics of the 1/8 inch active gage and the 1/4 inch compensating gage.

Tank 1 was cycled from 0 - 300 psig ten times while the gages were pressure calibrated using both the internal 350 ohm dummy in the strain indicator and a gage on tank 2 as the dummy. Typical calibration

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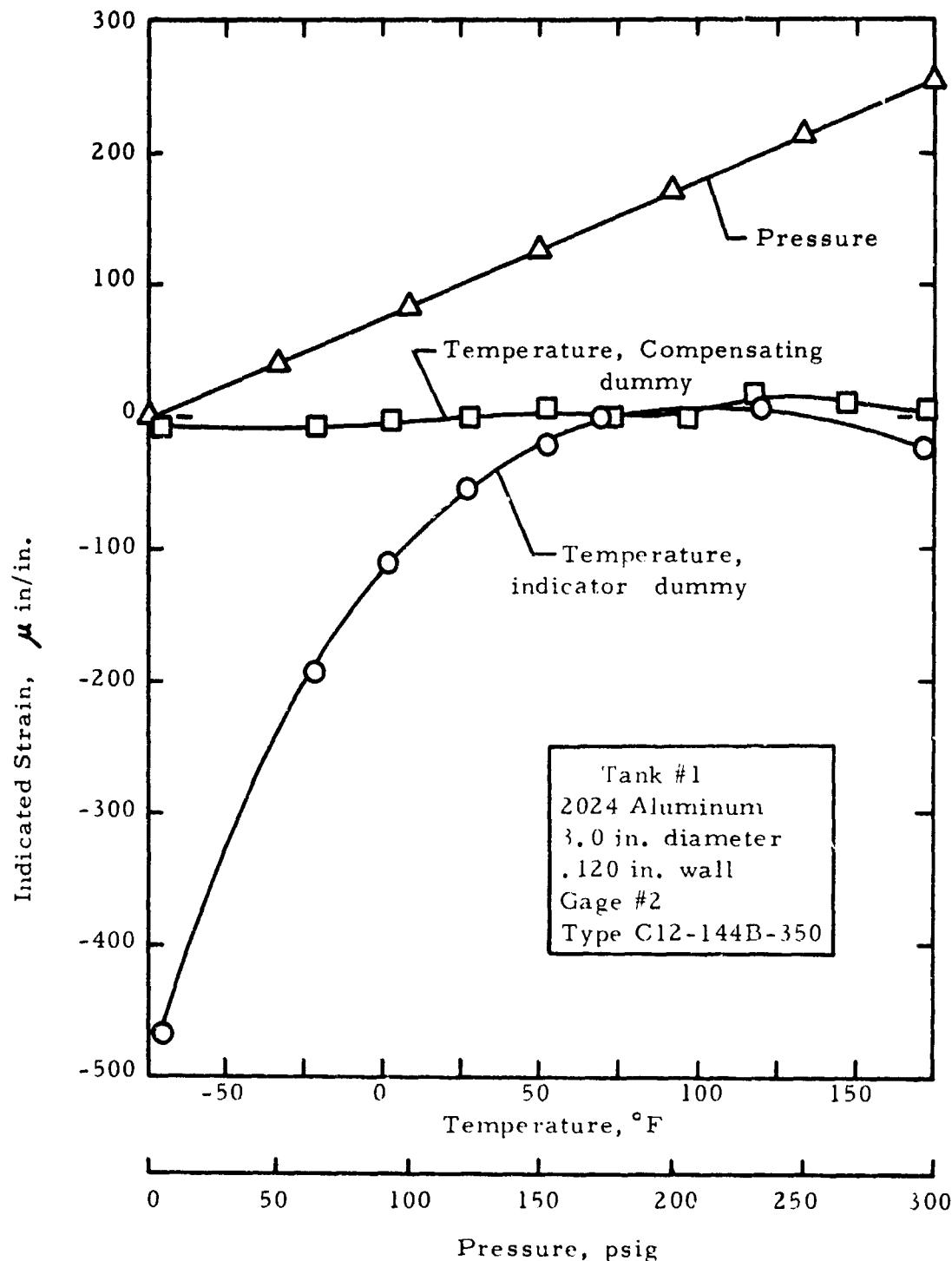
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Figure 9. Indicated Strain for Foil Strain Gage Attached With GA-2

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points using the internal dummy are given in Table X (pg 41) and the points are plotted in Figure 9 (pg 39) for gage 2. The indicated strain did not deviate more than  $\pm 1$  microin./in. from cycle to cycle during the calibration and the results were essentially linear. A calibration taken 10 days later after several temperature cycles is shown in Table X for comparison. The 1/4 inch gage (Gage 2) is very reproducible and the 1/8 inch gage (Gage 3 and 4) are not quite as consistent. A set of calibration data is also included for Tank 2 which has a larger strain for the same internal pressure due to both the larger tank diameter and the thinner tank wall.

In addition to pressure and temperature effects on the indicated strain, a third factor to consider is the variation of the gage zero balance over a long period. If the tank, gage or adhesive creeps to relieve internal pressure or temperature induced stresses, the balance point will change. In the pressure and temperature calibration tests, the gages were rebalanced before each calibration, but this cannot be done in a long term storage application. Each gage is balanced by adjusting a ten-turn potentiometer on the strain indicator or the switch and balance unit. The potentiometer on the strain indicator has a counting knob to permit accurate resetting of the balance position, so the zero balance drift can be determined by successive readings of the balance position. The gage zero-balance values, as noted prior to each calibration, are shown in Table XI (pg 42). The 1/4 inch gages show a random fluctuation on successive readings. In comparing the zero balance drifts over this short time period, the 1/4 inch gages appear more reliable than the 1/8 inch gages.

Typical data from tank 4 for gage 3 are shown in Figure 10 (pg 43). The same type of strain gages were used in Figure 9 and 10, but the GA-61 epoxy adhesive was substituted for the GA-2 adhesive in Figure 10 and a thinner wall, larger diameter tank was used. The temperature curves are similar in both figures, but the larger diameter, thinner wall tank produces about three times as much strain for the same internal pressure.

The zero balances were slightly more stable on tanks 3 and 4 using the GA-61 adhesive than on tanks 1 and 2 using the GA-2 adhesive. This is probably due to the higher temperature cure for the GA-61 epoxy. Therefore, the GA-61 was chosen for the Phase II strain gage application.

#### b. Temperature Sensors

The S44-50 temperature sensors were mounted perpendicular to the tank axis on tanks 3 and 4 to measure the apparent error in the temperature indication due to the internal pressure under the worst orientation condition. From 0 - 300 psig, the indicated strain change was 138 microin./in. for tank 4 and 28 microin./in. for the thicker wall tank 3, but this is equivalent to only 1.38 and 0.28F respectively. With the temperature gages mounted parallel to the tank axis on tanks 1 and 2, the temperature error was less than 0.05F. For the Phase II tests, the temperature error was less than 0.2F for a 500 psig pressure change.

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**TABLE X**  
**STRAIN GAGE CALIBRATION**

Tank Gage	Pressure (psig)					
	50	100	150	200	250	300
Tank No. 1*	Strain (microin./in.)					
Gage 2	43	85	126	170	213	255
3	43	84	130	175	221	266
4	40	80	123	164	207	247
Tank No. 2**						
Gage 1	45	88	132	176	220	263
2	42	85	127	160	212	254
3	46	91	126	182	226	270
4	42	84	125	167	211	250
Tank No. 2**						
Gage 1	118	236	350	468	582	700
3	109	226	337	452	564	679
4	106	218	326	438	549	661

**Notes:**

Gage 1 and 2, Budd C12-144B-350, 1/4-in. foil gage  
 Gage 3 and 4, Budd C12-124A-350, 1/8-in. foil gage

\*First group taken 11/21/66;

\*\*Second and third group taken 12/1/66.

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TABLE XI  
GAGE ZERO BALANCE VALUES\*

Date	Tank No. 1				Tank No. 2		
	Gage				Gage		
	1	2	3	4	1	3	4
11/21	----	8.02	5.59	4.90	----	----	----
11/22	----	8.03 8.96	5.57 5.27	4.91 4.38	7.74 7.70	6.34 6.38	2.74 2.91
11/23	8.96 8.94	7.98 7.95	5.27 5.29	4.36 4.36	7.70 7.69	6.38 6.36	2.92 2.91
11/28	8.93 8.98	8.01 8.03	5.27 5.31	4.28 4.44	7.69 7.72	6.42 6.44	2.98 3.00
11/29	8.94	8.01	5.27	4.38	7.70	6.42	2.97
11/30	8.94	8.00	5.26	4.38	7.70	6.41	2.98
12/13	8.95	8.00	5.64	4.45	7.71	6.46	3.06

Gage 1 and 2, Budd C12-144B-350, 1/4-in. foil gage.  
Gage 3 and 4, Budd C12-124A-350, 1/8-in. foil gage.

\*Readings on ten turn potentiometer (maximum of 10.00)

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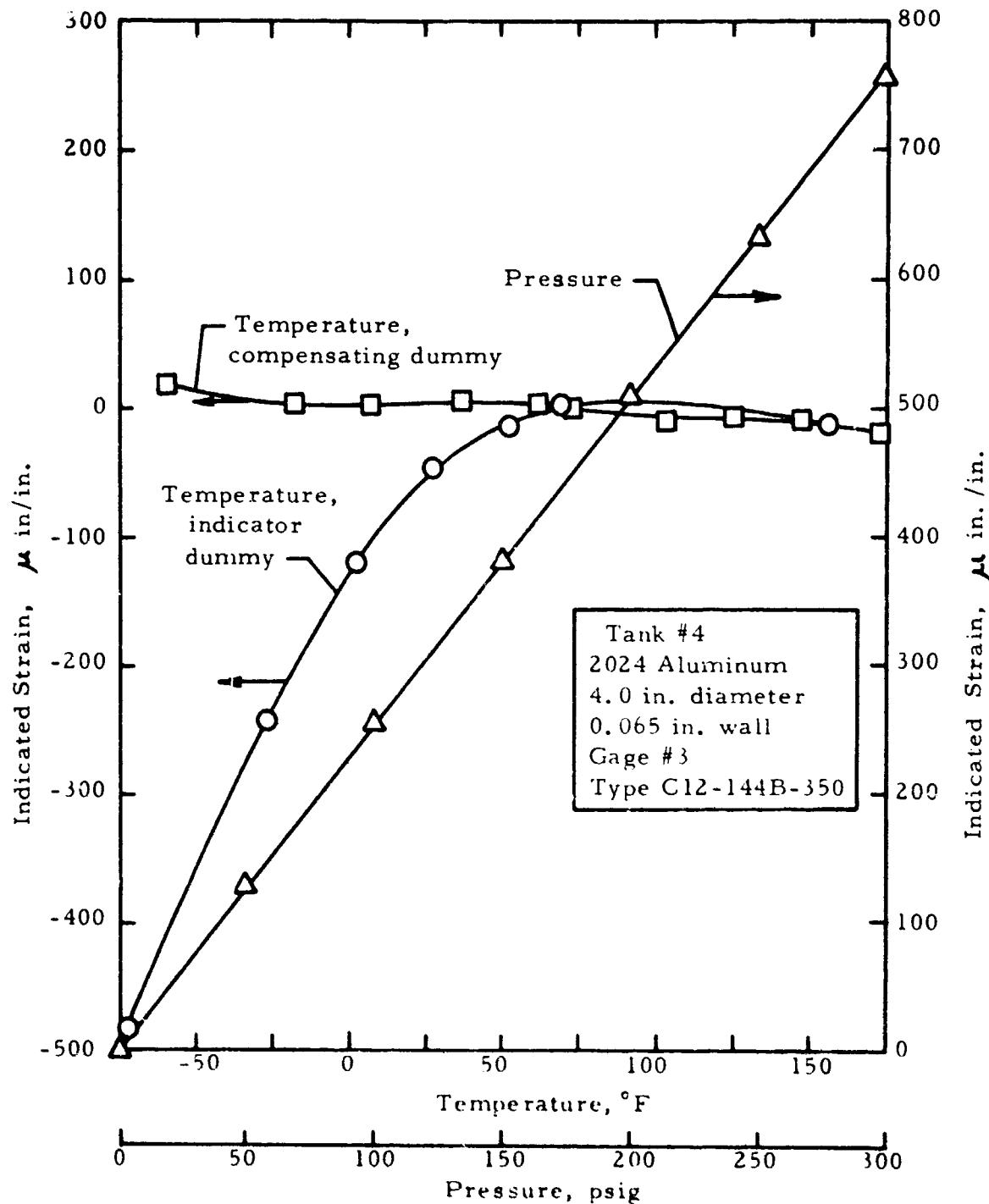
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Figure 10. Indicated Strain For Foil Strain Gage Attached With GA-61

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**UNCLASSIFIED**c. Semiconductor Gages

One set of dual element semiconductor gage data is plotted in Figure 11 (pg 45). Two of the four semiconductor gages were damaged during mounting, but the other two produced similar data. The gage factor for these gages is 250 which exceeds the capability of the strain indicator for a direct reading by a factor of 25. A gage factor of 5 was used and all strain readings were divided by 50 to find the true strain. Despite the temperature compensation built into the dual element gage, the apparent strain due to temperature change is over 700 microin./in. from -65F to +175F. The characteristic curve was very reproducible over several temperature cycles and a pressure reading could be corrected for the apparent strain due to temperature. Some of the apparent strain is due to a variation in gage factor which is specified as a 14% change per 100F. Due to the high cost of the semiconductors (\$45 for the dual element gage used here) and the adequate sensitivity of the foil gages, no further work was done with the semiconductors.

d. Wire Gages

The combination of a wire strain gage and Rokide bonding was suggested by Baldwin-Lima-Hamilton for long term stability which would be superior to a glued installation. Typical results with a 1/2 inch aluminum compensated gage are shown in Figure 12 (pg 46). The temperature compensation using two similar gages is not quite as good as for the foil gages in Figure 10 and 11 (pg 43 and 45 respectively). The Rokide application process is not as adaptable to field installation of gages as an epoxy glue which requires no special equipment. Similar gages on tank 6 must have been damaged during application and could not be used.

5. Material Selection

The strain gage equipment evaluated in this phase of the program was judged satisfactory for monitoring the storage of MHF-5. A more sophisticated readout instrument would be desirable for an eventual application to reduce the time required for monitoring multiple channels of data. The long-term stability, accuracy, and reliability of strain gage installations can only be demonstrated by a long test period under the specific environmental conditions, but the following comparisons can be made from the month of testing.

The foil gages applied with epoxy, wire gages applied with Rokide and semiconductor gages applied with epoxy all produced linear, repeatable strain calibrations when the tanks were pressurized internally. Temperature compensation was best with the foil gages, but the other gages showed a reproducible temperature calibration which could be used to correct pressure induced strain indications. The foil gages were chosen for further work because of the much higher cost of the semiconductor gages and the more difficult process of applying the wire gages with Rokide.

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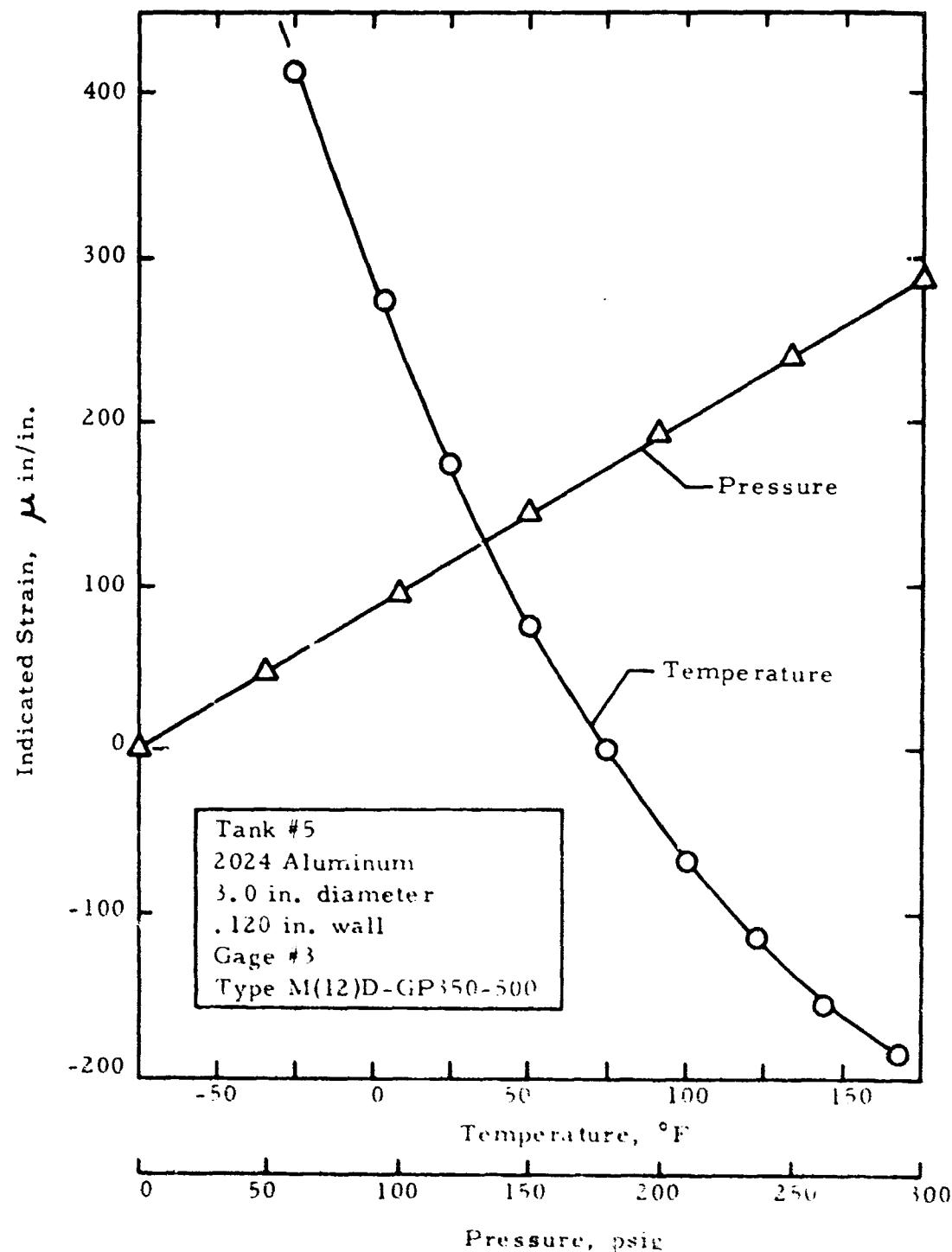


Figure 11. Indicated Strain for Semiconductor Gage Attached With GA-61

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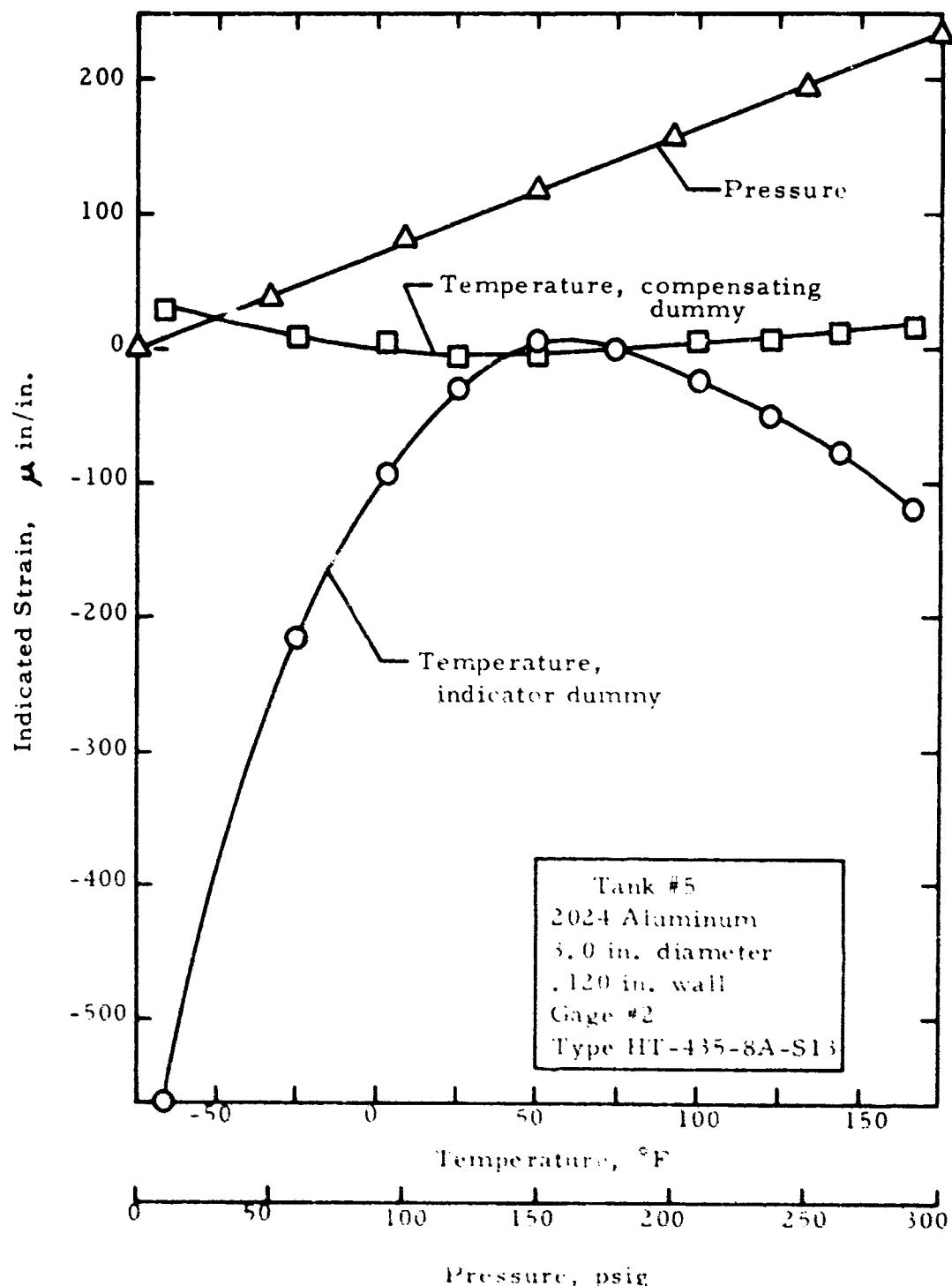
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Figure 12. Indicated Strain for Wire Strain Gage Attached With Rokide

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With the foil type gages, the longer gage length exhibited a more stable zero balance after temperature cycling. The GA-61 adhesive also appeared to be slightly less prone to creep at higher temperatures. The GW-5 waterproofing compound is impervious to water submergence. Therefore, these materials were chosen for the prototype tests.

### C. Thermal Conductivity Measurements

The purpose of this task is to demonstrate a leak detector probe suitable for warning of the presence of Compound A or MHF-5 vapors due to corrosion pinhole leaks or other failure modes in missile propellant tankage. Ideally, the leak detector should be of universal application and could monitor an area inside the missile or could monitor a closed environment such as a silo. Since a truly universal detector is nonexistent, a literature survey was conducted of potential detectors and the thermal conductivity cell was selected as most desirable for the missile application with these propellants.

#### 1. Literature Survey

A literature survey was made of leak detection measurement techniques and twelve of the most promising methods were studied in some detail and evaluated. The twelve methods were rated for twelve factors to obtain an overall rating factor as shown in Table XII (pg 48). The evaluation of each characteristic is designated as (1) good potential, (2) moderate potential, and (3) poor potential. The last column, rating factor, is a summation of the ratings for each leak detection technique. As a first approximation, the leak detection technique with the lowest rating factor number is the most desirable for this application unless the importance of a particular characteristic might outweigh a low rating factor. For example, the selectivity of the chemical indicators might warrant their use in certain applications in spite of a higher overall rating factor than other methods. From this table, the thermal conductivity technique is best suited for our use.

A detailed summary of the literature survey is included as Appendix B of this report. The complete discussion will be repeated in this section only for the selected thermal conductivity probe and the other techniques will be summarized briefly.

#### a. Thermal Conductivity

For a number of years, thermal conductivity was almost the exclusive method for leak detection because of its response to a large variety of solute vapors, its adequate sensitivity, linearity, and basic simplicity. The sensitivity is almost unlimited since almost any change of gas composition could readily produce a measurable effect.

This type of analyzer employs a Wheatstone bridge circuit to measure the difference in thermal conductivity between two gas compositions. A schematic of a four filament cell is shown in Figure 13 (pg 49). A fila-

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TABLE XII  
EVALUATION OF CANDIDATE LEAK DETECTION TECHNIQUES

Requirement Technique	Versatility	Adaptability to Specific Design	Sensitivity	Reliability	Evaluation Factors						Rating Factor	
					Ability to Withstand Environmental Conditions	Safety	Cost or Availability	Ease of Automation and Remote Sensing	Life Expectancy	Maintenance	Ruggedness	
Thermal Circuitry	1	1	2	1	1	1	1	1	1	1	1	13
Computerized Analyses	1	4	1	1	2	2	2	1	2	2	1	29
Electroacoustic Techniques	1	1	1	1	3	1	3	3	3	3	3	31
Electrochemical Techniques	1	1	1	1	1	2	2	3	3	3	3	31
Electromagnetic Techniques	1	1	1	1	1	2	2	1	3	3	3	31
Electrokinetic Techniques	1	1	1	1	1	2	2	1	3	3	3	31
Electrostatic Techniques	1	1	1	1	1	2	2	1	3	3	3	31
Hydrodynamic Techniques	1	1	1	1	1	2	2	1	3	3	3	31
Optical Techniques	1	1	1	1	1	2	2	1	3	3	3	31
Pressure Techniques	1	1	1	1	1	2	2	1	3	3	3	31
Radioactive Techniques	1	1	1	1	1	2	2	1	3	3	3	31
Vibration Techniques	1	1	1	1	1	2	2	1	3	3	3	31
Water Techniques	1	1	1	1	1	2	2	1	3	3	3	31
Other Techniques	1	2	1	1	3	1	3	3	3	3	3	32

1 - Good Potential

2 - Moderate Potential

3 - Poor Potential

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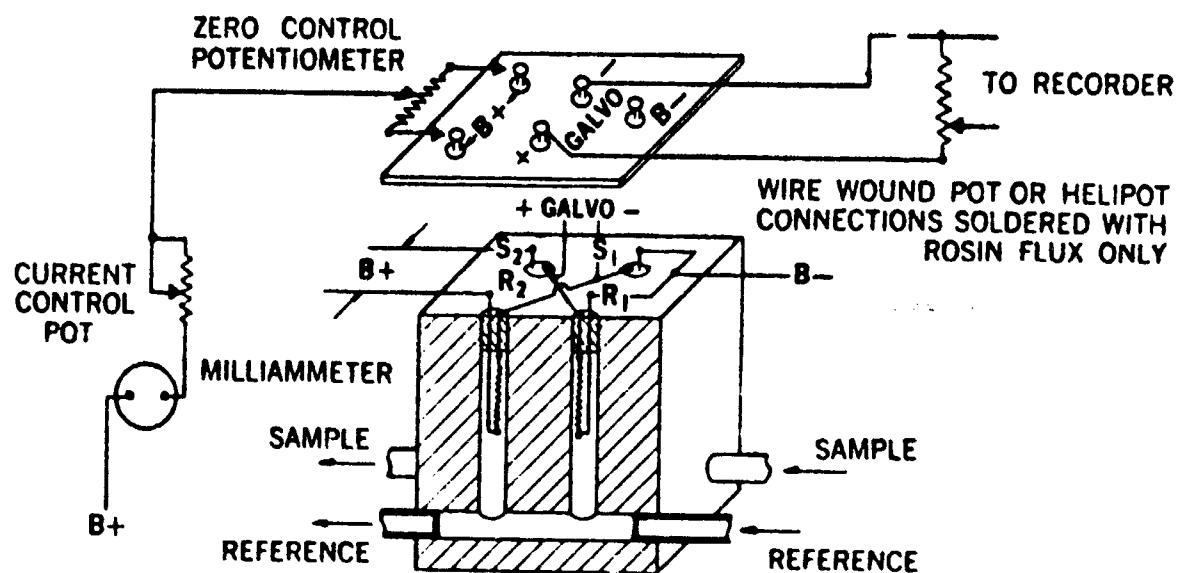
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Figure 13. Thermal Conductivity Schematic for 4 Filament Cell

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ment in each cell block is heated when power is applied to the bridge circuit. The heat is conducted from the filament to the side walls of the cell block by the air or gas surrounding the filament. As a result, the temperature of each filament is determined by the thermal conductivity of the air or gas. Since the electrical resistance of each filament is directly related to its temperature, which depends on the thermal conductivity of the gas, measuring the resistance with the Wheatstone bridge indicates the relative thermal conductivity of the gases in the two cell blocks. With the same gas surrounding all filaments, the bridge will be balanced by equal resistances in both arms. As the gas composition changes in the sampling well and remains constant in the reference well, the bridge becomes unbalanced to the extent determined by the change in sample composition.

These detectors employ either a heated metal filament or a thermistor for the sensing resistance element. The detectors are fast, sensitive and accurate for continuously recording gas or smoke concentration, composition and mixtures. The samples required are small, operation is continuous, and the apparatus will have a long life barring mechanical damage or corrosion.

The cost of an analytical installation is determined principally by that of the electrical instruments and machining used in conjunction with it. The first cost of calibration and interpretation is large in comparison with the cost of construction. The cost of thermal conductivity kits is \$500 to \$1000. They are manufactured by Beckman Instruments, Gow-Mac Instrument Co., Perkin-Elmer Corp., Varian Aerograph and Mine Safety Appliance Co.

A visit to the Gow-Mac Instrument Company in Madison, N. J., confirmed that thermal conductivity is practical for this application. Additional pertinent information for our specific application follows:

The safety aspect is good because the expected temperature of the filaments is below the flash point of either Compound A or MHF-5 vapors. If necessary, flame arrestors can be incorporated.

Sensitivity should be adequate for these propellants and there is a degree of selectivity because of the differences in thermal conductivity of MHF-5 and Compound A vapors.

Normal convection should be sufficient to sample the environment without using an air pump.

Operational temperature ranges should cause no difficulty for silo application of this device. Some temperature compensation would be required for field conditions where extremes in temperature would be encountered.

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**UNCLASSIFIED****b. Other Detectors**

The other eleven leak detectors were not considered as desirable for the current application. Specific drawbacks for the various types are specified as follows:

Mass spectrometry, infra-red spectrometry and ultraviolet spectrometry methods are not applicable due to high cost and lack of simplicity, ruggedness, and ease of automation and remote sensing.

Chemical indicators, colorimetric titration and electro-conductance techniques are undesirable in the area of automation and remote sensing, reliability and simplicity.

Ionization detectors have a poor life expectancy and the electron capture is not applicable to hydrazine fuels.

Flame ionization and clathrate methods can be eliminated because of safety considerations alone.

Condensation nuclei method is not applicable from the standpoint of adaptability to missile design, selectivity, simplicity, etc.

Microwave and combustion gas analyzers are not sensitive enough. Hot wire combustion techniques need oxygen, which may not be available in this application.

Other methods which were not considered because of insufficient potential were sound velocity, flow impedance, surface potential and capacitance cell.

**2. Equipment**

The apparatus for evaluating the thermal conductivity cell, as shown in Figure 14 (pg 52), consisted of a stainless steel vacuum rack, a 4.5 ml stainless steel cylinder and a 8850 ml aluminum cylinder to which the cell was attached. The thermal conductivity cell was a Gow-Mac TC Model 9454 which consisted of a stainless steel body with tungsten filaments. The reference side of the cell was hermetically sealed with one atmosphere of nitrogen at room temperature. The power supply and recorder were designed for a Kromo-Tog Gas Chromatograph Model K-2 made by Burrell Corporation of Pittsburgh, Pa. The cell current available with this unit is 80 - 130 ma and the strip chart recorder has a range of 0 - 10 mv.

The general test procedure was to connect the propellant and compressed gas lines and evacuate the entire apparatus. A sample of fuel or oxidizer was admitted into the small calibrated volume and the temperature and pressure noted. The measured fuel or oxidizer was transferred

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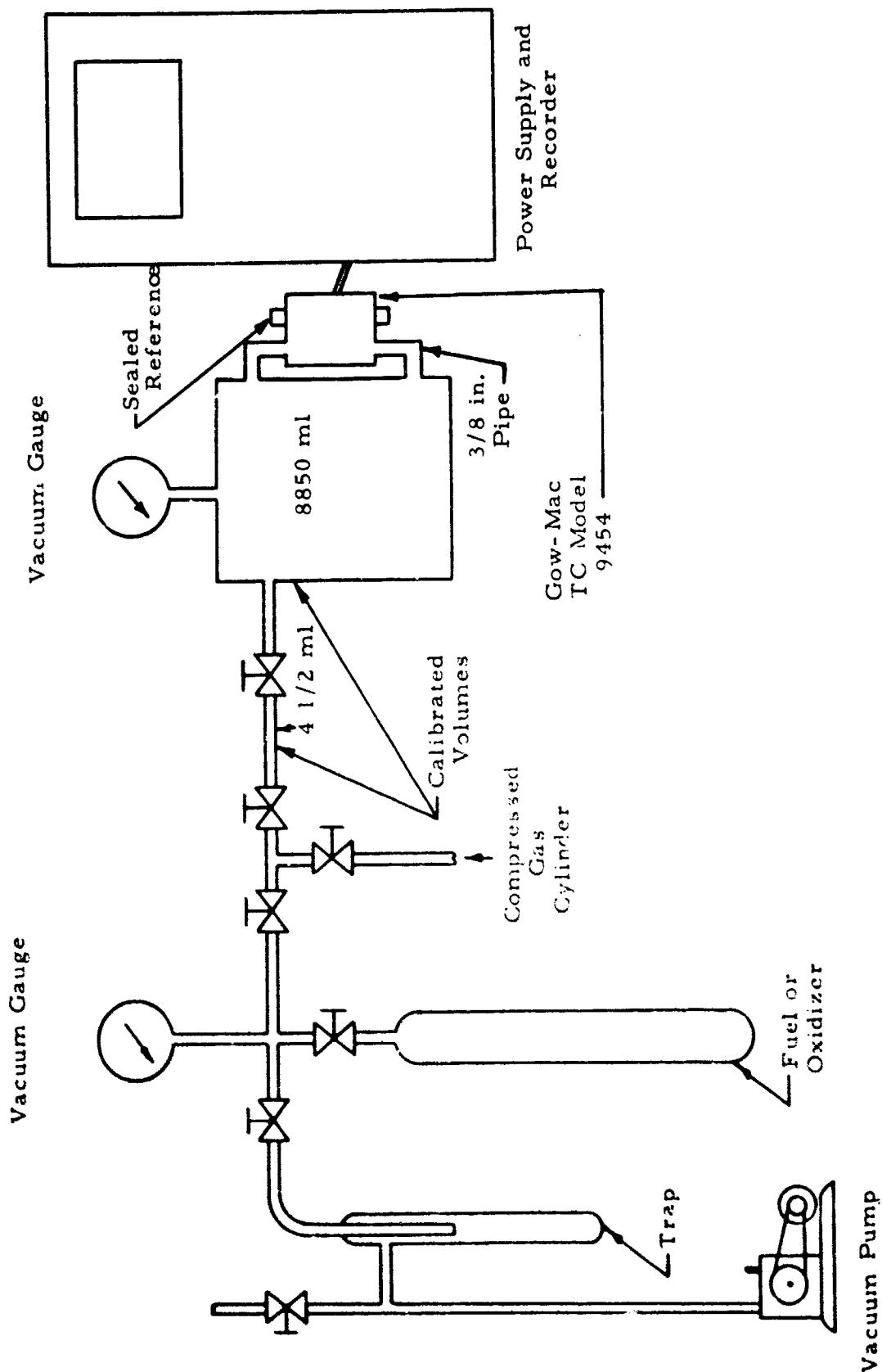
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Figure 14. Schematic of Thermal Conductivity Cell Apparatus

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to the large calibrated volume by flushing the small calibrated volume with nitrogen. Enough additional nitrogen was added to the 8850 ml volume to bring the pressure up to one atmosphere and the temperature was noted. The thermal conductivity cell signal was then recorded for the particular concentration and cell current. The expected life of the filament in the thermal conductivity cell is proportional to the required filament current, so the minimum current necessary for detecting small concentrations is important.

### 3. Test Results

The output of the thermal conductivity cell was measured using both Compound A and MHF-5 over a range of concentrations. These data are shown in Table XIII (pg 54) and are plotted in Figures 15 and 16 (pg 55 and 56).

For both the Compound A and MHF-5 tests, the carrier and make-up gas was nitrogen. All measurements were taken at room temperature and one atmosphere pressure.

The Compound A tests in Figure 15 were made at cell currents of 80 and 104 ma. Small concentrations, down to 33 ppm, were easily detected and it appears that smaller concentrations are detectable, but the recorder could not discriminate signals below 1 mv. Also, the 80 ma current is higher than necessary for good sensitivity, but the power supply could not be reduced below this level. As would be expected, the 104 ma current produced a larger output signal than the 80 ma current for corresponding propellant concentration. The zero millivolt position corresponds to a pure nitrogen sample at 760 mm pressure and room temperature which is measured against the nitrogen reference at the same conditions.

The MHF-5 tests in Figure 16 differ from the Compound A tests in two ways. The thermal conductivity cell is much less sensitive to MHF-5 and the minimum concentration measured was 37' ppm. Also, increasing the current in the cell increased the signal in a positive direction for the MHF-5. This provides a method of selecting which propellant is being detected by observing the output as signal current is increased. A possible explanation of this signal reversal is that fuel decomposition occurs at the higher filament temperature. The decomposition products, such as hydrogen, would cause a deflection in a direction opposite that of MHF-5 relative to nitrogen. It is known that gases such as hydrogen and helium give positive detector signals and this was verified with a lithium on this program.

### 4. Discussion

The thermal conductivity cell can detect the presence of Compound A and MHF-5. Unfortunately, limitations in the auxiliary apparatus limited the investigation of the detector sensitivity, but limited selectivity

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TABLE XIII

## RESULTS OF THERMAL CONDUCTIVITY CELL TESTS

Propellant	Filament Current ma	Signal mv	Concentration ppm
Compound A	80	- 1	33.4
		- 3.5	66.8
		- 7.5	100.2
		-12.2	116.9
Compound A	104	- 2.1	33.4
		- 6.5	66.8
		- 12.5	100.2
MHF-5	80	- .7	1562
		- .8	3127
		- 1.2	6250
		- 1.4	8330
		- 1.7	11100
		- 2.3	14800
		- 3.0	19760
MHF-5	120	+ 1.0	371
		+ 1.0	741
		+ 1.7	1472
		+ 2.2	2960
		+ 2.7	5920
		+ 4.0	11840
		+ 4.8	23700

Note: Carrier and make-up gas are nitrogen, all measurements taken at room temperature.

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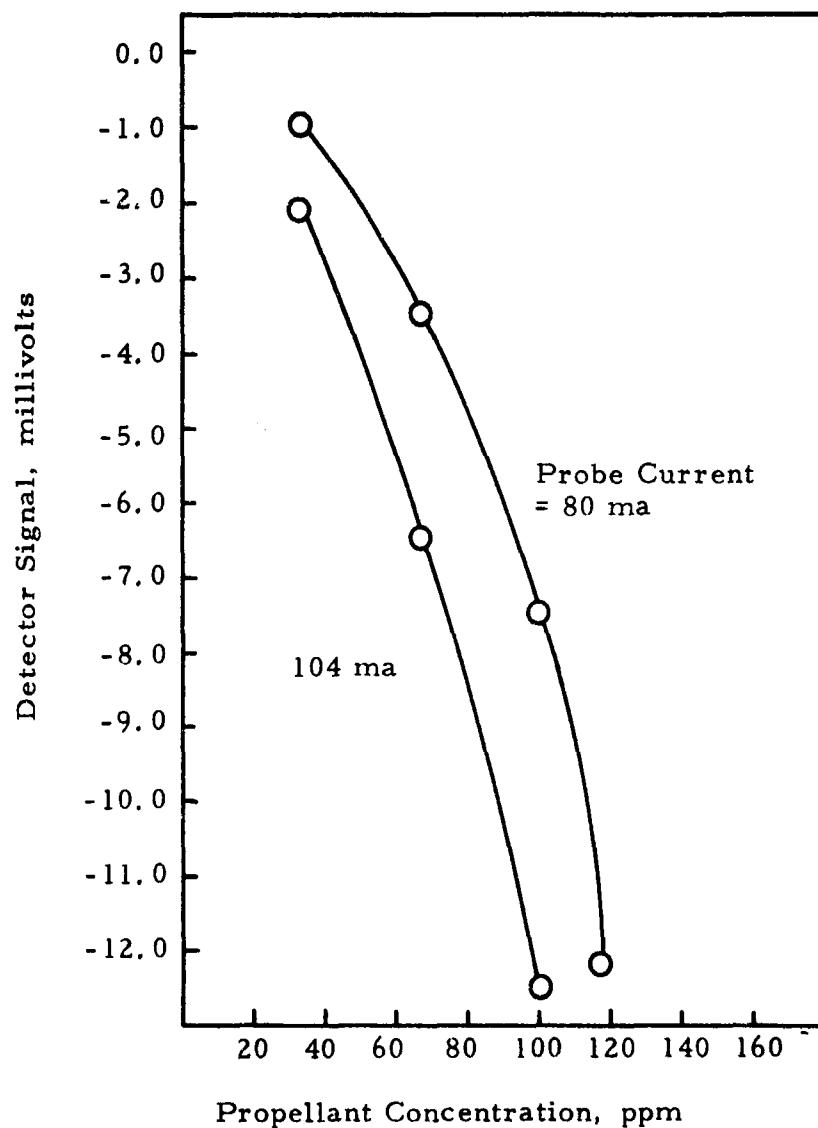
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Figure 15. Thermal Conductivity Tests with Compound A

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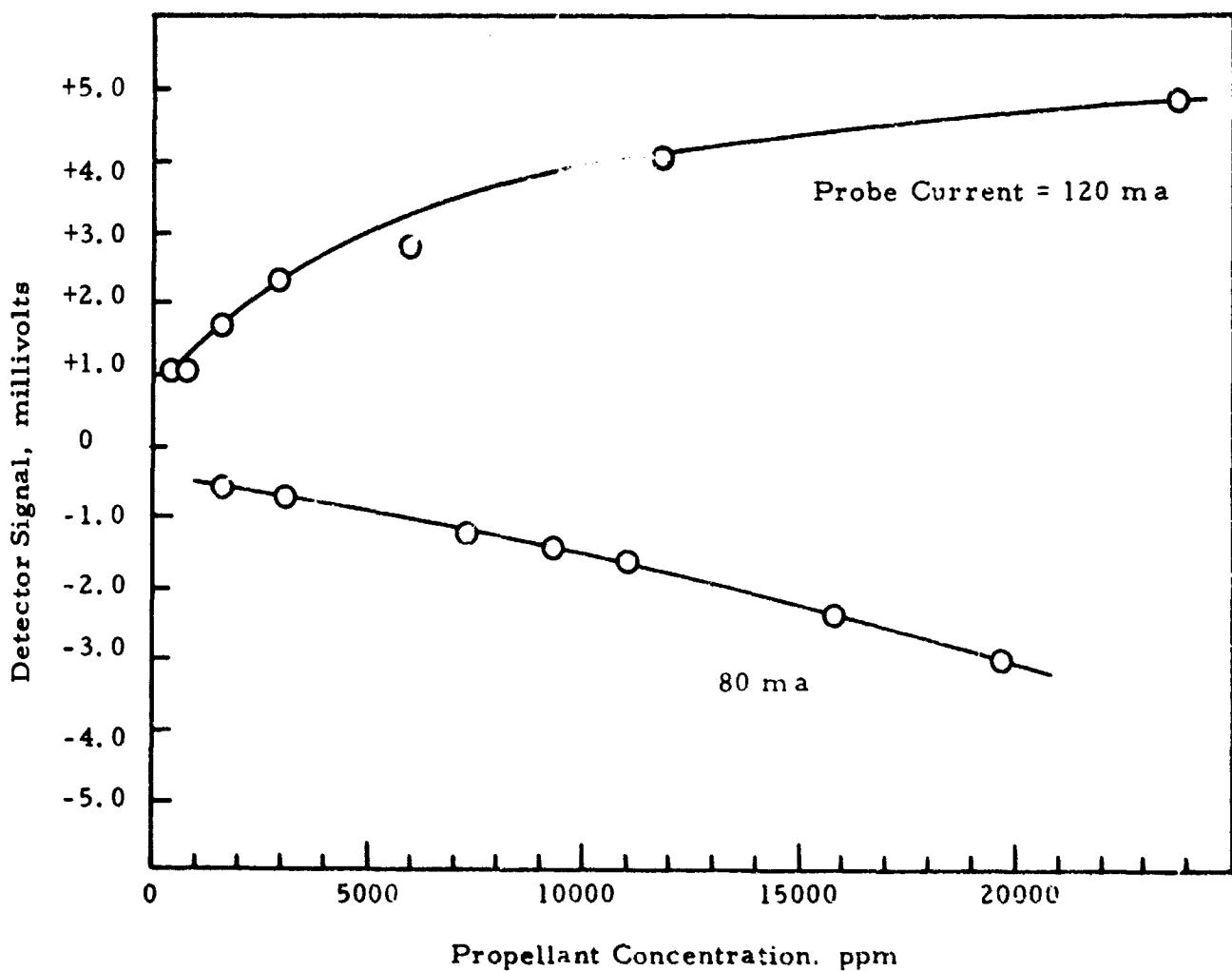
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Figure 16. Thermal Conductivity Tests with MHF-5

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between the two propellants was demonstrated. It was not possible to determine the minimum filament current necessary for Compound A detection or the minimum detectable MHF-5 concentration.

Several methods of optimizing the system are evident from these tests. A better power supply is needed with a range from 0 - 400 ma rather than the 80 to 120 ma limitation of the equipment used in these tests. The recording system must be improved to at least -0.1 mv sensitivity. Other tungsten filament designs will permit greater sensitivity or other filament materials, such as nickel, could be used. There appeared to be a reaction between the Compound A and the tungsten filament material as evidenced by a slight zero shift during the tests. The absolute values for Compound A may be in error, up to 1 mv. The MHF-5 tests, which were done after the Compound A, all returned to zero. Also, the thermal conductivity cell should be redesigned to mount inside the large volume to shorten the sample inlet line. With the cell used for these tests, the cell was mounted externally and connected with several inches of 3/8 inch tubing, which decreased the sample diffusion into the cell.

Additional tests are required to demonstrate sensitivity under more adverse operating conditions. The carrier gas was nitrogen in these tests. In application, the carrier would be air and other trace contaminants such as smoke or hydrocarbons might reduce the cell sensitivity.

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**PHASE II, TASK II, PROTOTYPE EQUIPMENT EVALUATION**

The Phase II, Task I work, which has been reported in Section IV, established the feasibility of the ultrasonic monitoring techniques and strain gage techniques for evaluating the degradation effects to be expected from Compound A and MHF-5. The prototype equipment used to explore these techniques was evaluated with actual and simulant propellants in the final three month phase of the program. A detailed test plan, which was approved by the Air Force before starting the test period, has been included as Appendix C of this report. The equipment used and an abbreviated test program outline will be described in this section together with the results of the tests.

**A. Equipment**

The ultrasonic equipment consisted principally of the Sonoray 301 Flaw Thickness Tester and Digital Micrometer manufactured by Branson Instruments Incorporated. Thickness gaging of the propellant tank walls was accomplished with the 1/2 inch diameter dual element transducer. Propellant induced corrosion in the liquid and vapor space of the tank, sludge formation in the bottom of the tank and foreign material location were monitored with the 1/4 inch diameter single element transducer. In addition to these two moveable transducers, two fixed transducers were used to demonstrate the capability of a permanently attached transducer. The fixed transducers were dual-element, 1/4 inch diameter units which were coupled to the tank and held in place with RTV (room temperature vulcanizing) silicone rubber.

The strain gage equipment was the strain indicator and switch and balance unit from Budd Instruments. In addition, an interconnecting box was assembled to couple the two units, allow rapid changing of the gages being monitored and increase the speed of the strain and temperature reading operation. An electrical schematic of this unit is shown in Figure 17 (pg 60).

**B. Test Items**

Small scale propellant tanks were used to simulate an air launch missile application. This application has the most rigorous environmental conditions of the three general launch conditions which include silo launch and mobile launch as well as air launch. The methods of monitoring are applicable to all three launch modes. The air launch design parameters were based on the Bullpup B which has approximately a 17-inch diameter aluminum tank with a 1/4 inch wall thickness.

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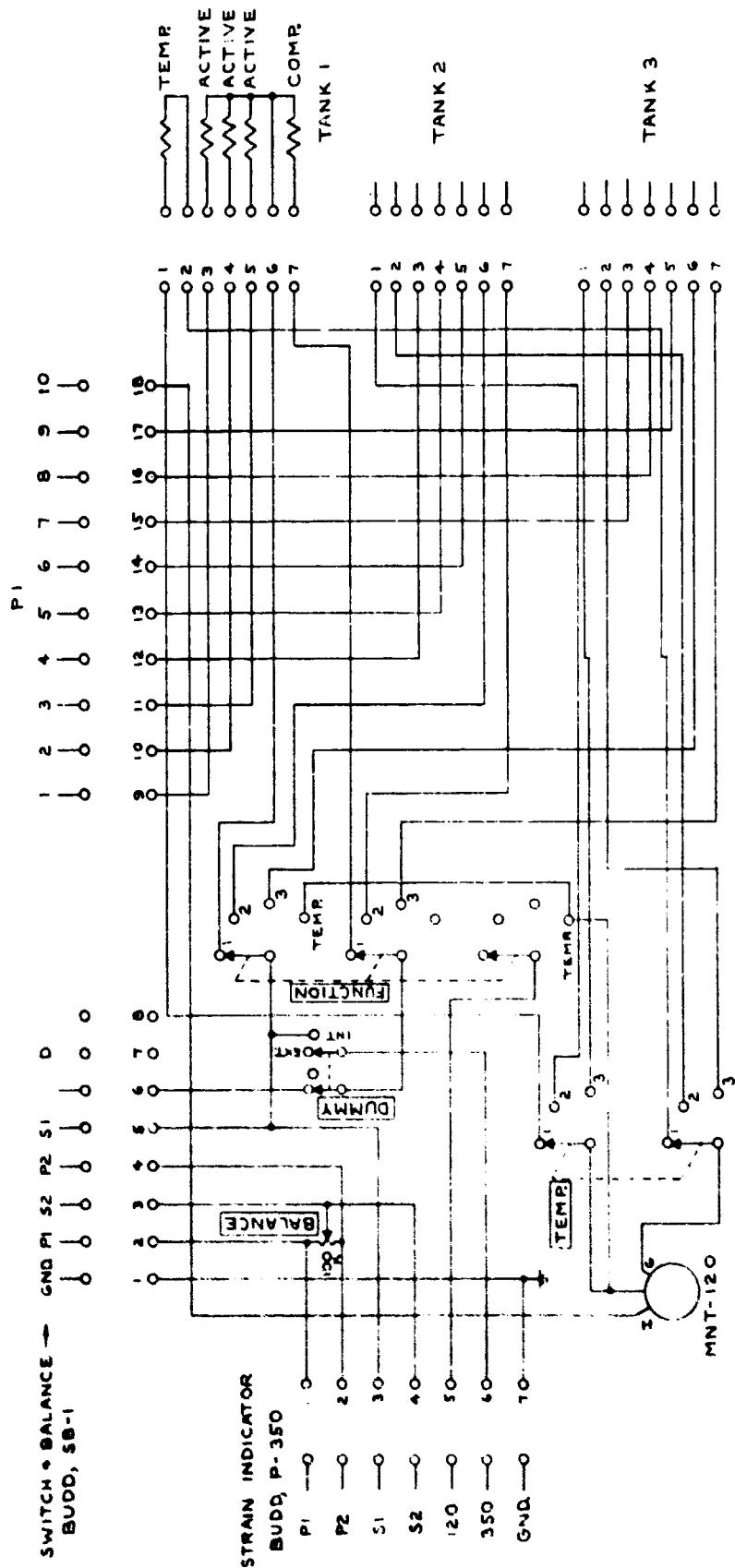


Figure 17. Schematic of Interconnecting Unit

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Aluminum tanks of 2024 with the actual 1/4 inch wall thickness were used for the ultrasonic tests. Some additional tanks were fabricated from 321 stainless steel to obtain comparative data with another tank material.

Since the test tank diameter was about 25 percent of the Bullpup diameter, additional aluminum tanks with a thinner wall (0.065 inch) were used for the strain gage tanks to duplicate actual stress levels. A few stainless steel tanks were included to accelerate fuel decomposition during the short three month test period.

All tanks are four inch outside diameter and six inch long. They were fabricated from 3-inch lengths of either the 1/4 or 1/16 inch wall tubing with flat 1/2 inch thick caps welded on one end. The end cap weld was made on the inside as well as the outside to eliminate cracks which could be difficult to thoroughly clean. The two halves were then circumferentially welded together to form the tank. The tanks for Compound A and MHF-5 were assembled with a 4-1/2 inch diameter Helicoid gage and a type MV 3004P Control Components valve as shown in Figure 18 (pg 62). These tanks are shorter than the tank described in Section IV.B.3 to limit the quantity of the propellant. Also, the internal welds were added to the tanks with propellant.

Some of the tanks, as specified in the next section, were instrumented with foil strain gages manufactured by the Budd Company. Temperature compensated gages were used with Type C12-144B-350 gages on the aluminum tanks and Type C9-144B-350 gages on the stainless steel tanks and type S44-50 temperature gages on both tank materials. Three of the strain gages were equally spaced around the tank 2-1/2 inch from the top end cap and oriented along the tank circumference to measure the hoop stress in the tank wall. A fourth gage was mounted on a separate segment of the same type of tubing as was used for the tank wall. This segment was taped to the tank so this compensating gage would experience the same temperature as the three active gages without any strain from internal pressure. In Figure 18, the compensating gage is below the number 7 and one of the active gages is between the number 4 and the wires at the center of the tank.

The gage wiring is indicated in the schematic of Figure 17 (pg 60). A temperature gage was also applied to each tank to indicate the wall temperature. The temperature gage was mounted parallel to the tank axis to minimize pressure-induced errors in the temperature reading. All gages were applied with a two-part epoxy, GA-61, supplied by Budd and waterproofed with another type two-part epoxy, GW-5. The seven wires from each tank terminated in a Cannon connector which mated with a receptacle on the interconnecting box. The strain gages and bourdon tube gages were calibrated from 0 - 500 psig at ambient temperature and the strain gages were also calibrated between +175°F and -65°F to correct for any incomplete temperature compensation.

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Figure 18. Propellant Tank, Gage, and Valve Assembly

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The strain gage pressure calibrations were treated statistically to establish the variation to be expected in the test readings. Each strain gage was calibrated from 0 to 500 psig in 50 psi steps for a total of 10 calibration points per gage. The indicated strain reading at each calibration step was divided by the pressure to obtain the factor, microin./in.-psi, which is shown in Table XIV (pg 64) for the gages on tanks 1A and 1S. The stainless steel tank factor averaged about 1/3 that of the aluminum tank due to the difference in modulus of elasticity of the two materials.

The standard deviation for each set of ten calibration points was calculated from:

$$\sigma = \sqrt{\frac{\sum X^2 - \frac{(\sum X)^2}{N}}{N-1}}$$

where  $\sigma$  = standard deviation  
 $X$  = calibration factor  
 $N$  = total calibration factors = 10

The coefficients of variation (percent variation) was calculated from:

$$V = \frac{\sigma}{\bar{X}} \times 100$$

where  $V$  = percent variation  
 $\bar{X}$  = average calibration factor.

For the stainless steel tanks, the percent variation ranged from 3 to 5% and for the aluminum tanks, it was 1 to 2%.

For these tests, each gage was individually calibrated. In a field application, it might be desirable to install a gage on a tank already filled with propellant, which was sealed, as in a prepackaged application, which could not be calibrated by pressurizing the tank. To calculate the variation between the separate strain gage installations, the strain readings at 500 psi were also treated statistically. For the 24 gages installed on aluminum tanks, the average strain was 1236 microin./in. at 500 psi and the coefficient of variation was 5.04%. The 27 gages on stainless steel tanks averaged 437 microin./in. and the variation was 12.3%. Thus the error would be 3 to 5 times greater with uncalibrated strain gages.

### C. Test Program

The 27 propellant tanks were used to store Compound A, MHF-5, dilute sulfuric acid and alcohol for 90 days. The number of each type of tank and the temperature conditions during the storage period are shown in Table XV (pg 65) for each liquid.

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**TABLE XIV**  
**STRAIN GAGE PRESSURE CALIBRATIONS**

Gage No.	Tank 1A			Tank 1S		
	1	2	3	1	2	3
Calibration, microin/in-psi	2.420	2.100	2.520	.8200	.8200	.8200
	2.500	2.137	2.630	.8500	.8500	.8500
	2.493	2.158	2.633	.8400	.8600	.8533
	2.505	2.163	2.625	.8350	.8400	.8500
	2.496	2.187	2.624	.8400	.8520	.8560
	2.493	2.189	2.610	.8366	.8466	.8500
	2.491	2.208	2.617	.8400	.8516	.8571
	2.507	2.214	2.615	.8425	.8500	.8575
	2.502	2.233	2.613	.8466	.8555	.8688
	2.496	2.223	2.602	.8540	.8600	.8720
$\Sigma X$	24.906	21.812	26.089	8.4047	8.4855	8.5347
$\Sigma X^2$	62.036644	47.59207	68.073177	7.064678	7.201597	7.285880
$(\Sigma X)^2$	62.030884	47.57633	68.063592	7.063898	7.200371	7.284110
deviation, S	0.0256	0.0418	0.0326	0.0279	0.0350	0.0421
% variation, V	1.03	1.92	1.25	3.32	4.22	4.95

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TABLE XV  
TANKS FABRICATED FOR PROTOTYPE EVALUATION

Propellant	Temperature °F	Tank Material	Wall Thickness in.	No. of Tanks
MHF-5	+175	2024 Al	0.065	2
	+175	321 SS	0.065	1
	-65 to +175	2024 Al	0.065	2
	-65 to +175	321 SS	0.065	1
	+60	321 SS	0.065	3
Compound A	+175	2024 Al	0.25	2
	+175	321 SS	0.25	1
	-65 to +175	2024 Al	0.25	2
	-65 to +175	321 SS	0.25	1
	+60	321 SS	0.25	2
Sulfuric Acid	-65 to +175	2024 Al	0.25	6
Alcohol	-65 to +175	2024 Al	0.065	2
	-65 to +175	321 SS	0.065	2

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The hydrazine-based fuels, such as MHF-5, generate gaseous products if they decompose during long term storage. Therefore, the strain gage technique was used for MHF-5, and all nine fuel tanks were instrumented with three active strain gages. From previous tests at TCC-RMD under Contract N0w 65-0575-c, pressure rises of 0.1 to 0.2 psi/day in aluminum and 2 to 4 psi/day in stainless steel tanks at +100F and 5% ullage could be anticipated. However, the decomposition rate is extremely temperature sensitive and at test temperatures of +175F used for this program much higher pressure rise rates were anticipated.

The primary concern in long term storage of Compound A is chemical attack of the tank wall which will result in thinning of the tank walls and possible deposition of sludge at the bottom of the tank. The ultrasonic equipment was used to monitor the eight Compound A tanks. Since the Compound A is compatible with both aluminum and stainless steel, the degree of corrosion was expected to be minimal in the three-month test period, so six additional aluminum tanks were filled with dilute sulfuric acid to better demonstrate the capabilities of the ultrasonic equipment. A typical corrosion rate from the literature for 40% sulfuric acid on 1100 aluminum is 1/4 inch per year at room temperature. Solutions of 30%, 40%, and 50% acid were used in each pair of tanks to vary the corrosion rate. The ultrasonic equipment was also used to monitor these tanks.

The four tanks with alcohol were used to try to accelerate the aging process of the installed strain gages. They were exposed to a series of test cycles including temperature shocks, vibration, humidity, and salt spray. The zero balance, resistance to the tank, and pressure calibration were checked periodically to evaluate any creep induced.

The tests with Compound A and MHF-5 were grouped into three temperature conditions. The highest expected ground storage temperature of +175F was used continuously to accelerate potential decomposition or corrosion; temperature cycling between +175F and -65F included the extremes expected for air launched missiles; and the tanks at +60F ± 20F were control tanks. The temperature cycling included two days per week at +175F, one day at -65F, and the remainder of the time at ambient temperatures of about 70F.

Three temperature controlled cabinets were set up and checked out for these tests. Two cabinets were maintained continuously at +175F to provide separate high temperature conditions for the fuel and oxidizer. The third cabinet could be mechanically cooled to -65F and was used on different days of the week for either fuel or oxidizer storage. These same cabinets were used for the sulfuric acid and alcohol tank tests.

#### D. Test Results

##### 1. MHF-5

The volume of each MHF-5 tank was determined with water and the tanks were loaded to a 5% ullage at the highest temperature expected

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for each tank (ambient or +175F). The ullage calculation was based on the tank volume and did not include the pressure gage tube or fittings on top of the tank, so the true ullage was slightly higher.

The nine fuel tanks were stored for 90 days as specified in the test plan. All strain gages were read five times per week for the entire test period rather than reducing the reading frequency to three times per week after the first two weeks as originally planned. This permitted evaluating the temperature cycled tanks at all three temperature levels each week and also increased the total data points.

The results of these tests have been plotted in Figures 19 through 27 (pages 68 through 76). The solid line connects the indicated pressure readings from the bourdon pressure gage mounted on each tank and the pressure scale is on the left side of the data plot. The three sets of data points, which are related to the right scale of the graphs, indicate the deviation of each of the three strain gages from the reference bourdon tube gage. To obtain these points, each of the three active strain gages were read on the strain indicator using the dummy gage on the tank. The strain reading was reduced to a pressure equivalent using the appropriate pressure and temperature calibration curve for the individual strain gage. The difference between the strain gage value and the bourdon tube gage reading is the deviation plotted in the figures with a plus deviation indicating the strain gage reading is higher. With the data plotted in this manner, the magnitude of the strain gage error can be seen and the trend of error with time is evident. The percentage error at any time can be calculated by dividing the deviation by the bourdon gage pressure. As can be seen from the figures, the errors are fairly constant and are independent of pressure level in the tank.

Aluminum tank 1A (Figure 19 - pg 68) was stored at a nominal +175F continuously for the 90 day period. The temperature controller was not very sensitive and the observed temperatures ranged between +160F and +190F. This is why the bourdon pressure curve is not smoother. Also, the occasional higher temperature excursions increased the decomposition of the fuel. This provided a more severe environment for the tests, but could give a distorted view of the storability of this particular fuel at the desired +175F. When the tank pressure approached 500 psig, the tank was vented to 0 psig and continued at +175F.

The data for day 6 and day 49 are suspect since the grouping of the three gages appears normal, but the entire set is out of the normal deviation. The random fluctuations from day to day are attributable to inaccuracy in reading the bourdon tube gage (5 psi scale graduations), varying contact resistances in the selector switches and connectors and inability to reproduce the zero balance settings on the strain indicator for each reading. These fluctuations are 15 to 20 psi total spread for this tank (1 psi = 2.1 microin./in. strain). Superimposed on the fluctuations is the drift with time or increasing pressure which is about 2 psi/mo. for the gages on this tank.

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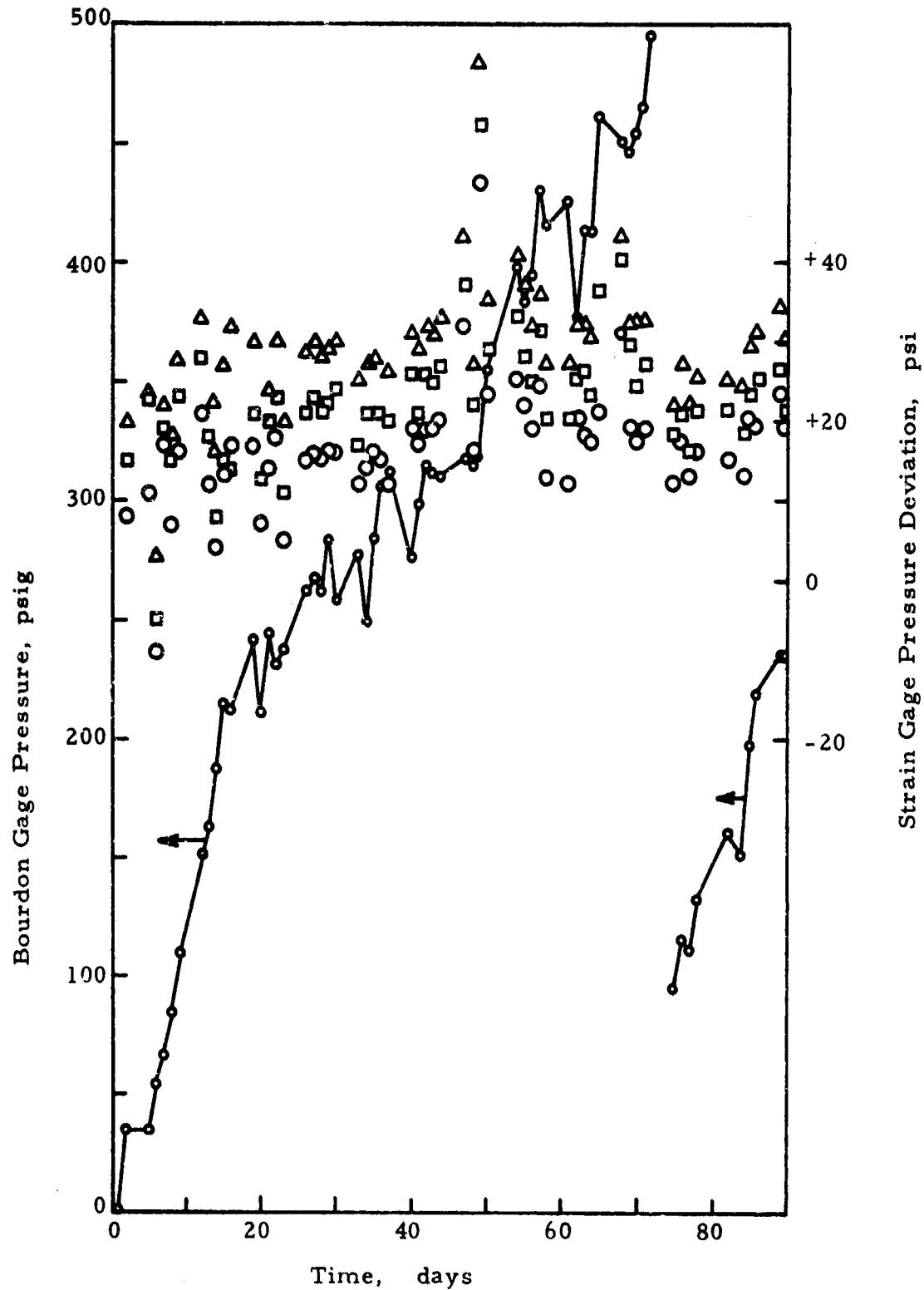
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Figure 19. Pressure History of Tank 1A with MHF-5  
at +175°F

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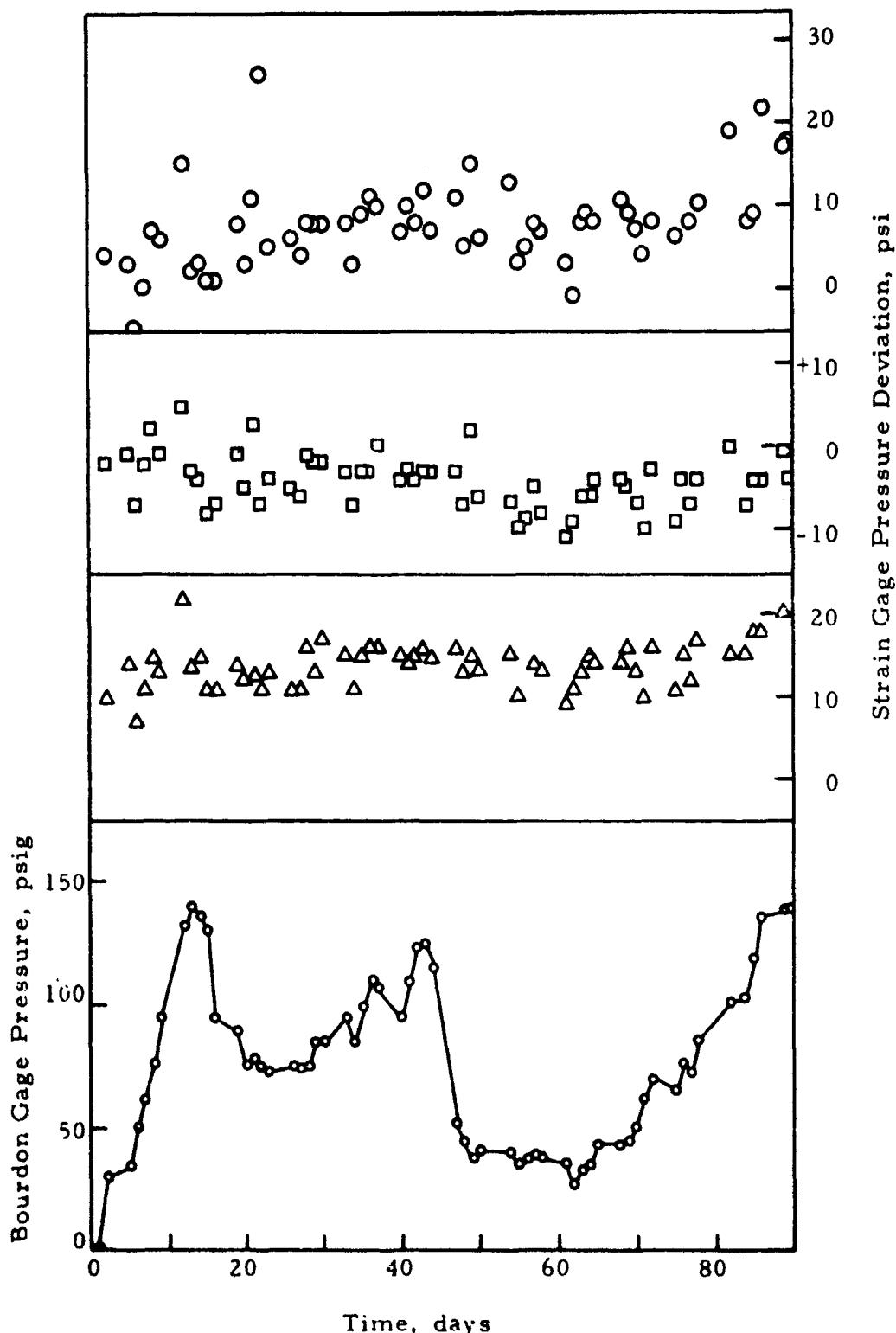
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Figure 20. Pressure History of Tank 2A with MHF-5  
at +175°F

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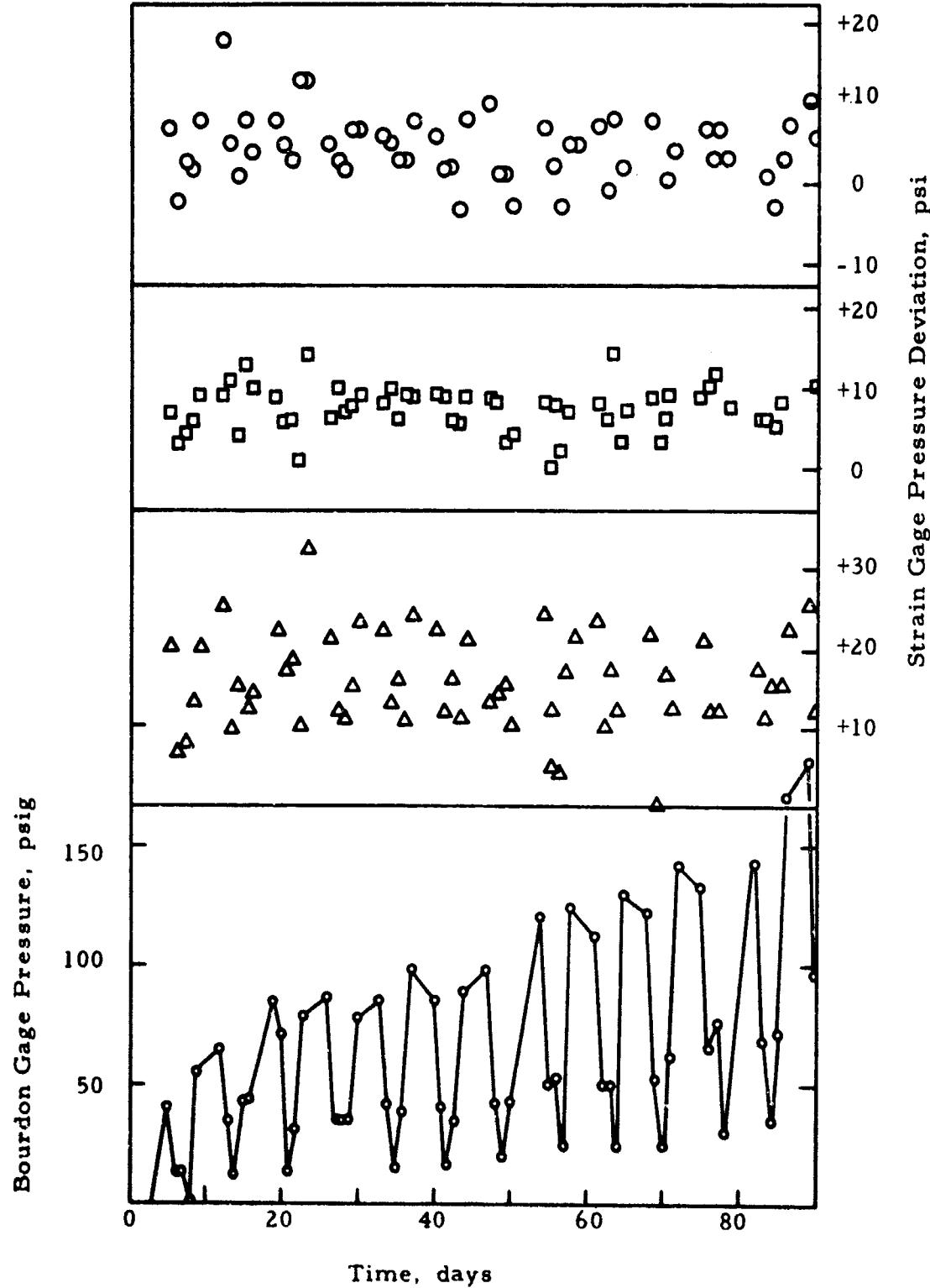
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Figure 21. Pressure History of Tank 3A with MHF-5  
Cycled Between  $-65^{\circ}\text{F}$  and  $+175^{\circ}\text{F}$

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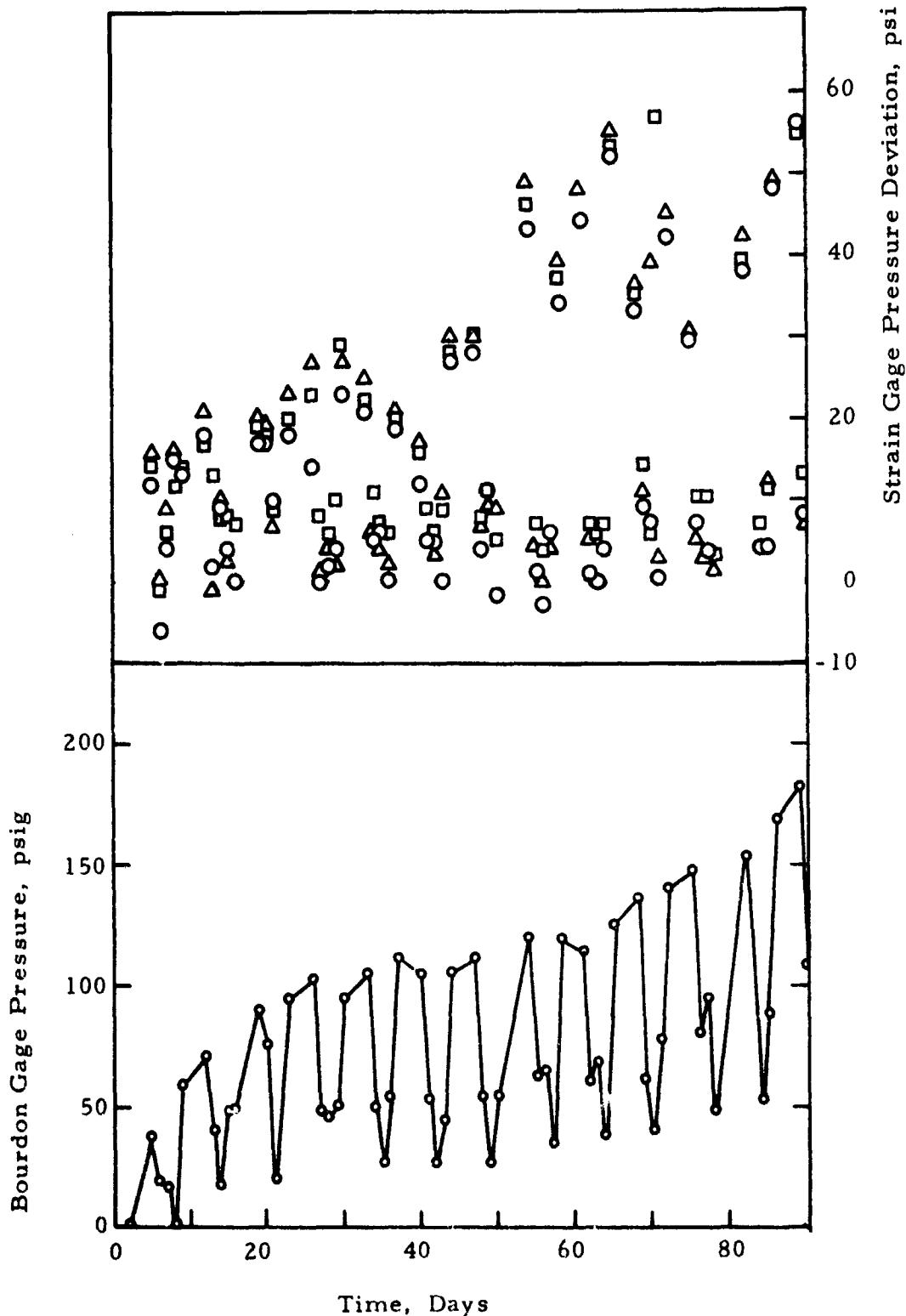
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Figure 22. Pressure History of Tank 4A with MHF-5 Cycled Between  $-65^{\circ}\text{F}$  and  $+175^{\circ}\text{F}$

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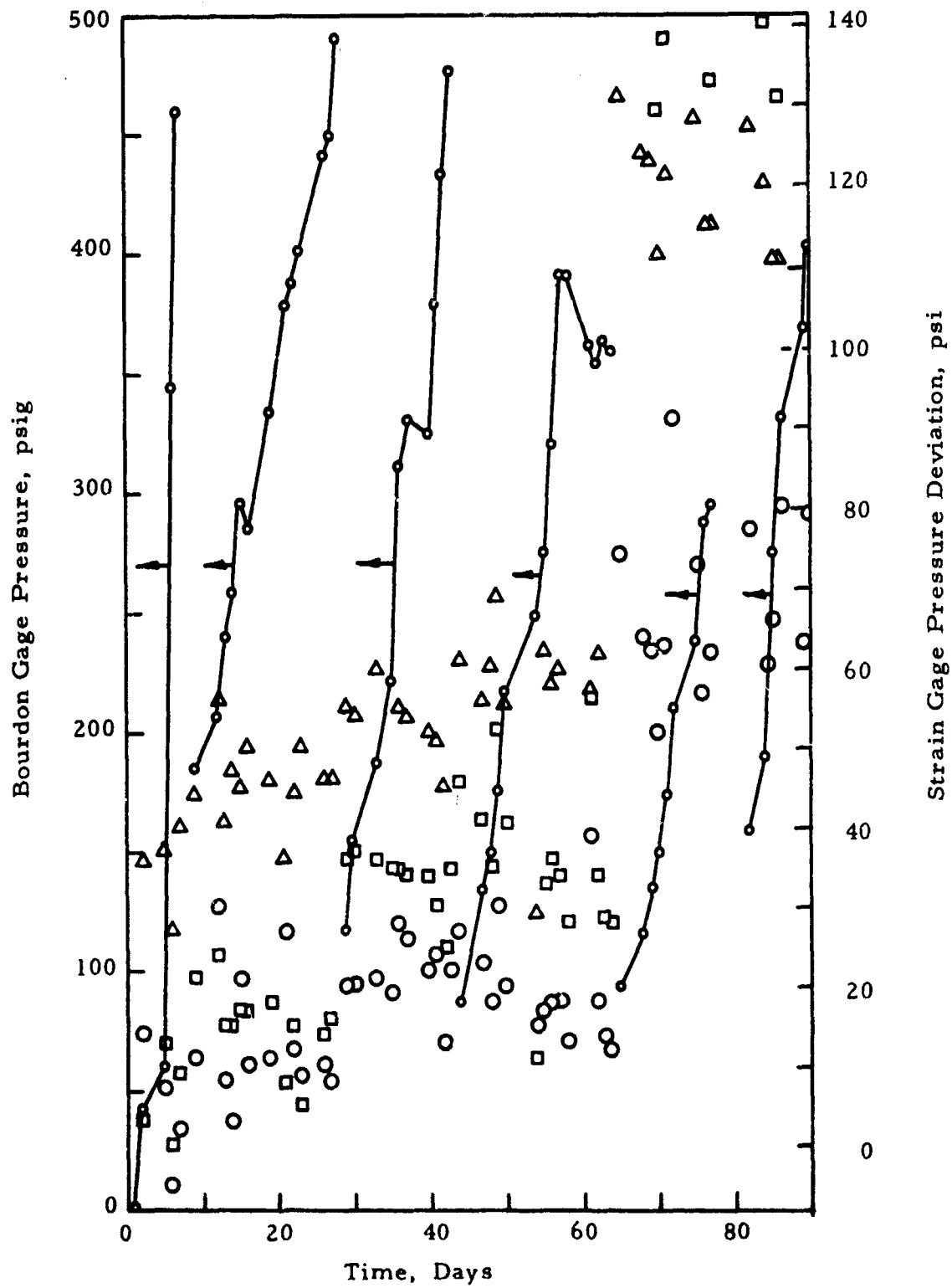
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Figure 23. Pressure History of Tank 1S with MHF-5 Cycled Between Ambient and +175°F

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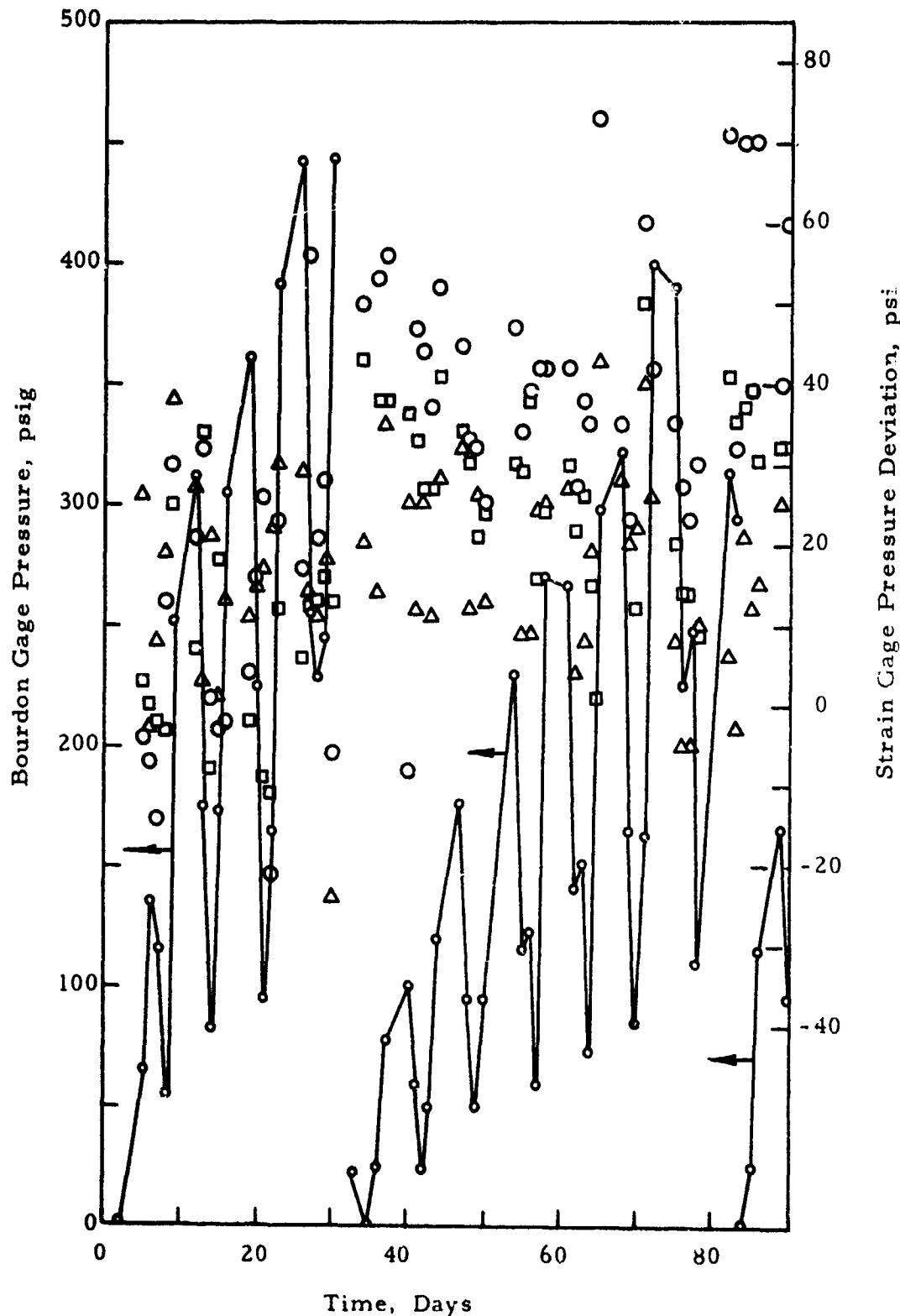
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Figure 24. Pressure History of Tank 3S with MHF-5 Cycled Between  $-65^{\circ}\text{F}$  and  $+175^{\circ}\text{F}$

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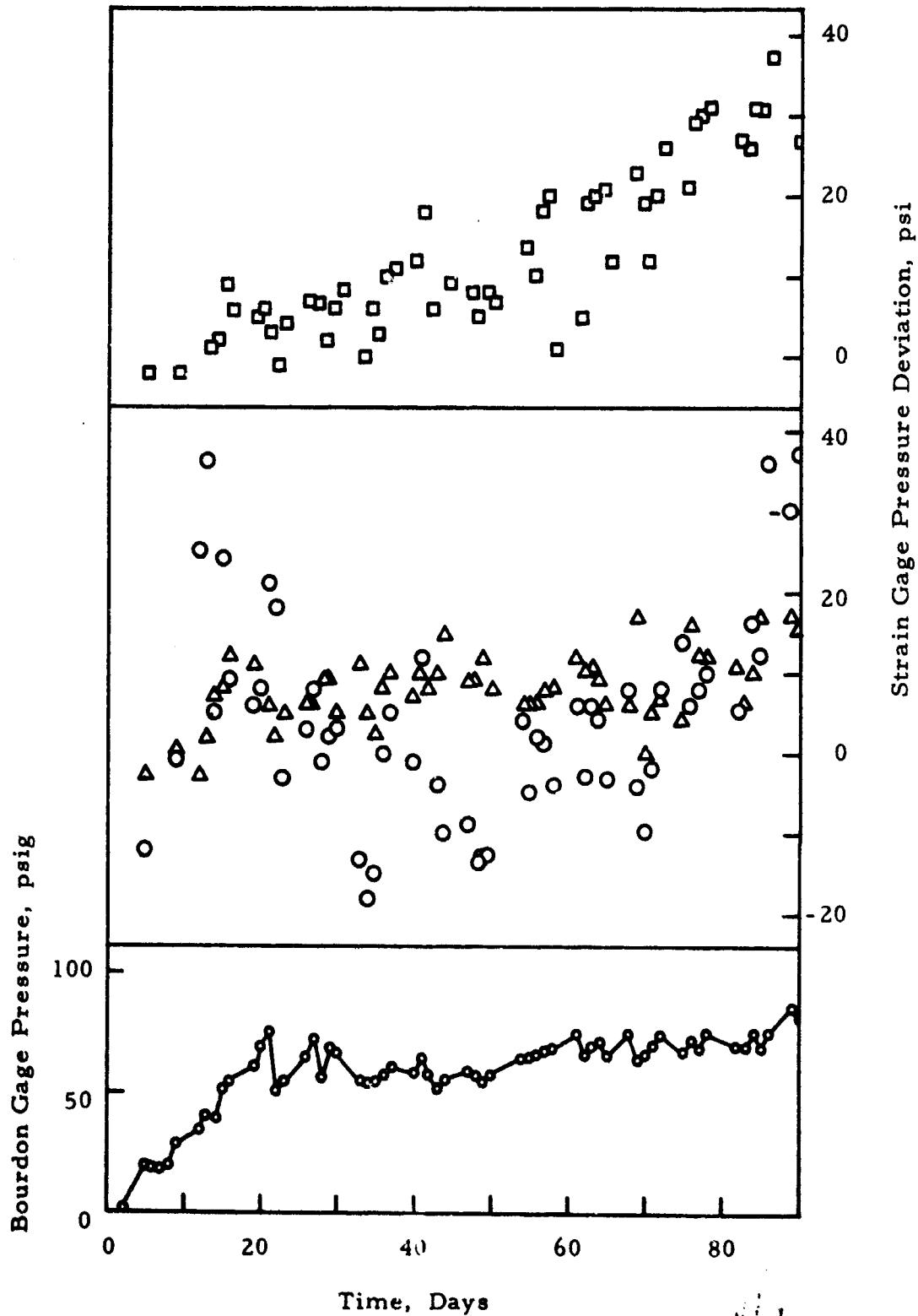
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Figure 25. Pressure History of Tank 2S with MHF-5  
at Ambient Temperature

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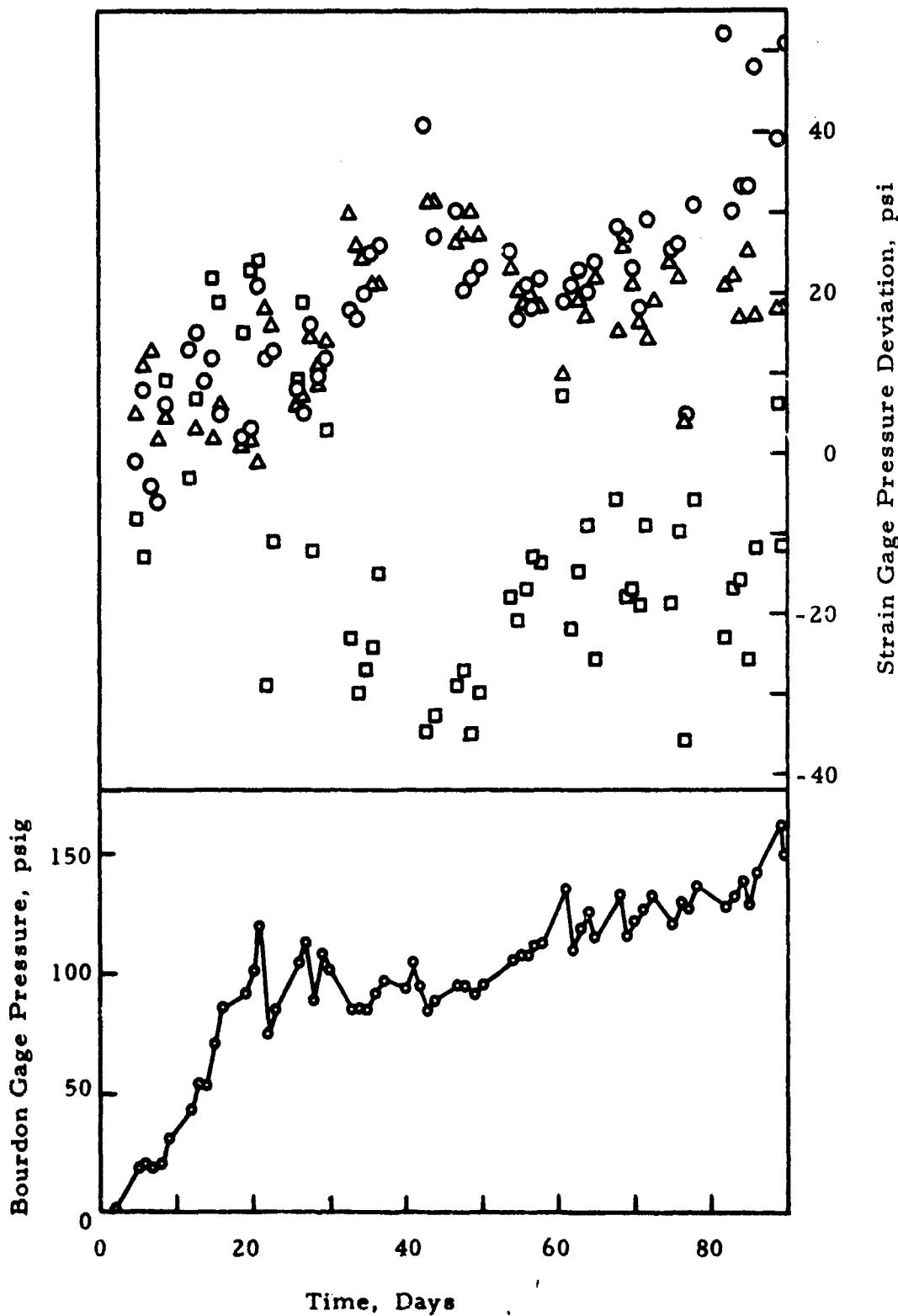
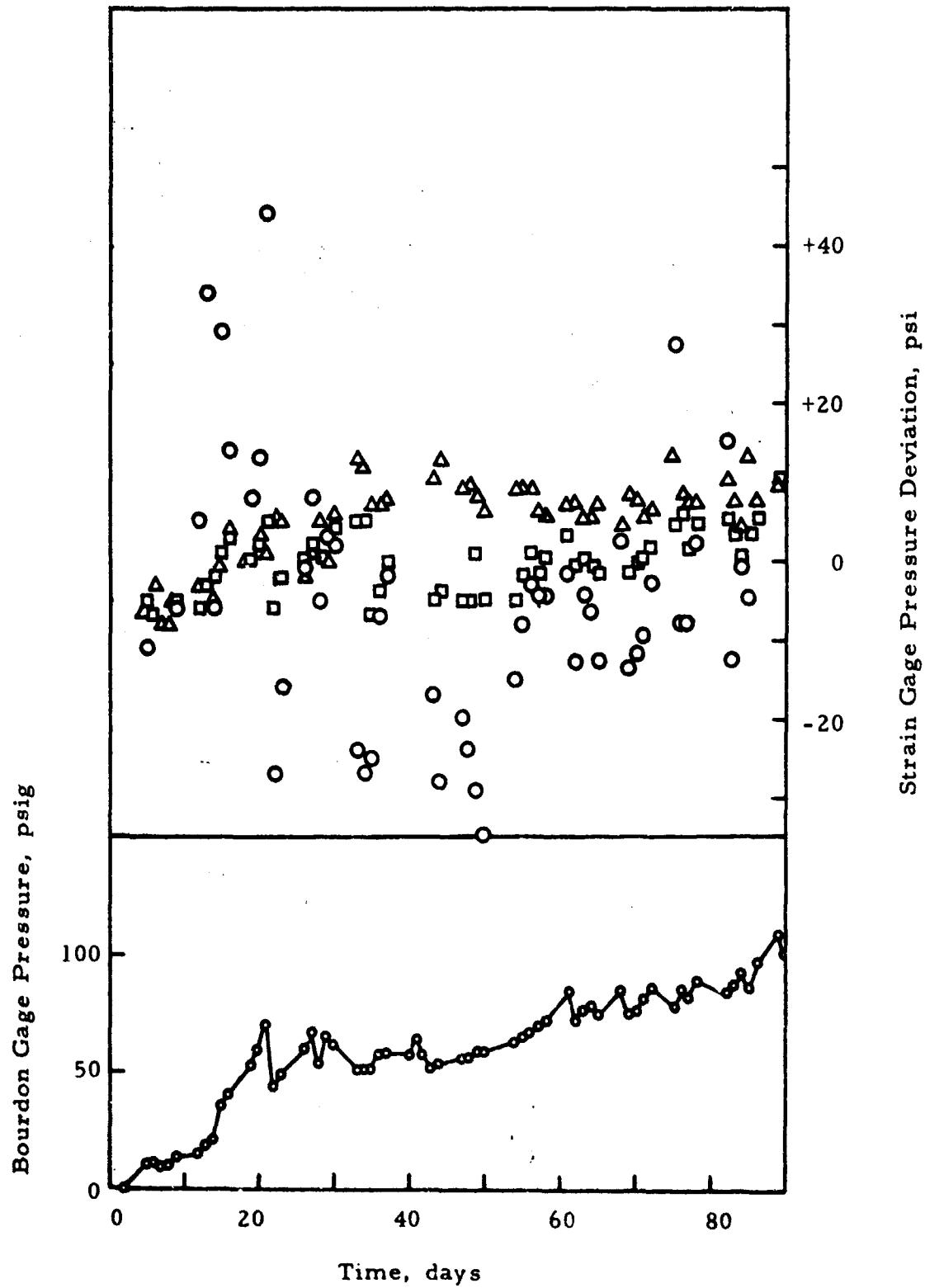


Figure 26. Pressure History of Tank 4S with MHF-5  
at Ambient Temperature

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**Figure 27. Pressure History of Tank 5S with MHF-5  
at Ambient Temperature**

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The errors are all positive starting with the initial readings. The data were reviewed by the strain gage manufacturer and the initial zero shift is probably attributable to incomplete stabilization of the gage installation prior to calibration. For example, transducer manufacturers apply the strain gage to the transducer diaphragm and allow the installation to stabilize for a month before initial calibration. The tanks in this project were calibrated within a week of gage application. A longer stabilization period before calibrating and loading the tanks might eliminate this problem.

Tank 2A (Figure 20, pg 69) was intended to be a duplicate of 1A, but it evidently developed a small leak which was undetectable with commercial leak detection solutions. It afforded the opportunity to evaluate strain gage drift at +175F with a more constant tank pressure. Daily fluctuations are less than 10 psi and drift is about 1 psi/month for this tank.

Tanks 3A and 4A (Figures 21 and 22, pgs 70 and 71) were cycled between +175F and -65F and readings were taken at +175F, ambient, and -65F on successive days producing the sawtooth type pressure curve. The bourdon gage on tank 4A tended to hang up, especially at the higher temperature and it appears that the bourdon gage indicated a low value at the high temperature resulting in all three strain gages indicating a high positive deviation. All deviations over 15 psi correspond to the high temperature condition and should be questioned for validity. Otherwise, both tank 3A and 4A have errors of the same magnitude as tanks 1A and 2A.

Stainless steel tank 1S (Figure 23, page 72) was originally scheduled to be stored continuously at +175F with tanks 1A and 2A. After 40 hours, the pressure reached 460 psig so the tank was vented to 0 psig and was subsequently stored at +175F for 7 to 7-1/2 hours per day, five days a week, and at ambient temperature the remaining time. All data were taken while the tank was at the higher temperature. Each succeeding time the pressure approached 500 psig, the tank again was vented to zero at ambient temperature.

The stainless steel and aluminum tanks were the same diameter and wall thickness, so the stainless steel exhibited 1/3 the strain for the same internal pressure. For an arbitrary amount of random strain fluctuation due to varying contact resistance and zero balance setting, the stainless steel will indicate three times as much pressure variation as the aluminum tank. This must be considered when comparing the data point spread with the stainless steel and aluminum tanks. Tank 1S has a larger data scatter than the aluminum tanks as would be expected from the preceding discussion. The drift is also higher than for the aluminum tanks and residual strain indications remain after the tank is vented to zero. This is particularly evident after the fourth venting when the pressure had exceeded the 500 psig gage range by 50 to 100 psig. In application to a missile, the tank would not be vented.

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(U) Tank 3S (Figure 24 - pg 73) was temperature cycled between +175F and -65F with tanks 3A and 4A except that 3S was held at +175F for 7 to 7-1/2 hours rather than 24 hours at each step. As was the case with 1S, tank 3S shows residual strain when vented at day 32. The drift with time was not as great as 1S.

(U) Tanks 2S, 4S, and 5S (Figures 25, 26, 27 - pgs 74, 75, 76) remained at ambient temperature for the entire period. The temperature was not controlled, but was expected to remain between 40 and 80F which is the temperature range for a conditioned mobile launch application. Actually the temperature exceeded 90F around day 20 and again between days 25 and 30 causing the minor pressure peaks.

(C) Before loading the propellant tanks, the fuel was analyzed as 18.2% HN, 54.9% MMH, 24.3% N<sub>2</sub>H<sub>4</sub>, 1.4% H<sub>2</sub>O, and 1.2% other impurities. Tank 1S was selected for post-test analysis to see how much the composition had changed due to the heating and to venting the tank five times. The analysis was 18.4% HN, 52.3% MMH, 24.7% N<sub>2</sub>H<sub>4</sub>, 1.1% H<sub>2</sub>O, 2.4% NH<sub>3</sub> and 1.1% other impurities. Evidently the hydrogen was vented off and some ammonia was left as a decomposition product. Also, the fuel changed from colorless to dark brown.

(U) The fuel tanks were emptied, flushed with water and recalibrated. Table XVI (pg 79) compares the initial and final zero balances and the strain reading at 500 psig. The zero balance values are the readings on a ten-turn potentiometer and represent the resistive balance necessary to null the bridge circuit with no strain on the gage. The internal balance uses the internal 350 ohm resistor in the P350 strain indicator to complete the bridge and the external balance uses the dummy strain gage mounted on the segment of tank material. Thus, comparison of the internal balances evaluates the change in each gage and comparison of the external balances evaluates each strain gage and dummy gage combination.

(U) While performing the final calibrations, the potentiometer on one channel of the switch and balance unit was found to be "noisy", particularly in the range used for the test program. The zero balance shifted when the potentiometer was tapped. This channel was used for the data represented by circles on the graphs for tanks 2A, 1S, 2S, 3S, 4S and 5S. The potentiometer is probably the reason for the odd fluctuations which are especially evident in Figures 25 and 27 (pg 74 and 76).

(U) In Table XVI, the internal balance generally shows a positive change for the tanks which were continuously at ambient temperature and a negative change for the tanks that were heated to +175F. All three strain gages on tanks 2A and 4A shifted more than 0.1, but the dummy gage reacted in the same direction and the external balance shift was less.

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**TABLE XVI**

**COMPARISON OF INITIAL AND FINAL STRAIN GAGE CALIBRATIONS**

Tank	Zero Balance				Strain at 500 psig. microin./in.	
	Internal*		External**			
	Initial	Final	Initial	Final	Initial	Final
1A	2.480	2.425	7.150	7.070	1248	1248
	2.595	2.600	7.345	7.290	1116	1118
	2.185	2.185	6.760	6.675	1301	1303
2A	1.880	1.705	6.330	6.230	1279	1285
	1.495	1.400	4.675	4.655	1293	1304
	1.860	1.705	6.275	6.235	1300	1314
3A	1.440	1.410	4.010	3.975	1248	1244
	1.735	1.685	5.455	5.415	1172	1171
	1.655	1.610	5.130	5.100	1169	1168
4A	1.920	1.815	6.140	6.120	1078	1076
	2.440	2.270	7.190	7.155	1214	1211
	2.020	1.905	6.430	6.415	1242	1244
1S	1.850	1.835	5.115	4.950	427	416
	1.780	1.735	4.835	4.535	430	424
	1.865	1.845	5.185	5.000	436	427
2S	1.900	1.910	4.230	4.130	464	458
	2.000	2.000	4.560	4.485	418	416
	1.575	1.585	3.140	3.120	421	420
3S	1.410	1.400	2.850	2.800	407	395
	1.990	1.990	5.050	4.990	478	422
	1.790	1.805	4.340	4.350	470	464
4S	1.845	1.850	5.415	5.335	395	392
	2.895	2.965	7.400	7.405	452	452
	1.585	1.600	4.310	4.270	520	516
5S	2.730	2.790	7.185	7.175	441	438
	1.855	1.880	5.350	5.120	584	582
	2.100	2.135	6.135	6.110	500	500

\*Internal zero balance - uses 350 ohm resistor in strain indicator

\*\*External zero balance - uses 350 ohm dummy gage on tank

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As would be expected from Figure 23 (pg 72), the largest external zero balance shift was experienced by tank 1S. The calibration changed about 2% so the large pressure deviation was entirely due to zero shift. It would appear from the internal and external balance number that the shift was principally in the dummy gage rather than the three active gages.

## 2. Alcohol

One of the requirements for monitoring equipment which could not be demonstrated on this short program was a useful life of five years or longer. Potential problems with strain gages are creep in the tank, adhesive and/or strain gage itself, failure of the adhesive bond, or moisture decreasing the electrical resistance between the tank and the gage. The aging cycle was accelerated as much as possible by subjecting strain gages to all the anticipated environmental extremes.

Two aluminum and two stainless steel tanks were gaged for the accelerated life tests. The tanks were similar to the MHF-5 tanks and the same strain gages were used. Two sets of dummies and active gages were used on each tank for a total of twenty-four active gages on the four tanks. The calibrations for these active gages were included in the statistical analysis of gage variation. The tanks were filled with alcohol, leaving 5% ullage, to avoid using propellant in the vibration facilities.

A test cycle was established in the test plan. The steps included an initial 24 hour soak at +175F following the calibration. The tanks were temperature shocked between -65F and +175F by moving them from an oven to a cold box and back again ten times. They were vibrated at 1.4 g's and 35 cps for four hours at -65F and four hours at +175F. An additional eight hours of vibrations were made at 3 g's and 13 cps at ambient temperature. Then the tanks were stored at 100% humidity and 120F for 48 hours.

Before starting the test cycle and after each of the six steps in the cycle, the indicated strain was read with no pressure on the tanks to determine the stability of the zero point. The strain readings were converted to equivalent pressure values and are reported in Table XVII (pg 81). The larger apparent errors with the stainless steel tanks, 6S and 7S, are partially due to the larger psi/strain factor for the stainless steel.

After the 48 hours at high humidity, large strain changes at zero pressure were indicated by most of the gages. When the gage leads were soldered in place, a small pin point of solder was left on the connections. Evidently the three coats of waterproofing compound failed to completely cover the tip leaving a potential water leakage path. Water must have penetrated at this point and changed the joint resistance at the connection. Inspection of the last line of Table XVII shows that no more than 2 aluminum strain gages and 2 stainless steel strain gages were still usable. Even these

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TABLE XVII  
APPARENT PRESSURES FOR STRAIN GAGE LIFE TESTS

Test Condition	Tank 5A						Tank 6A					
	1	2	3	4	5	6	1	2	3	4	5	6
Start	-2	-2	-2	1	5	5	6	13	-3	0	3	
+175°F, 24 Hours	0	-1	-1	10	2	0	2	7	-7	10	0	12
+175°F to -65°F (10 Times)	-15	18	-20	-1	0	-2	11	7	-2	-3	-2	6
1.4 g's, 35 cps, 4 hr, -65°F	10	15	4	2	15	-2	4	24	-11	17	15	8
1.4 g's, 35 cps, 4 hr, +175°F	17	20	8	10	23	5	32	65	2	18	27	18
3 g's, 13 cps, 8 hr, amb.	15	19	7	10	22	2	32	65	-4	20	28	11
100% Humidity, 120°F, 48 hr.	>-500	>-500	>-500	>500	16.7	-25	462	35	-100	>-500	>-500	>-500

Test Condition	Tank 6S						Tank 7S					
	1	2	3	4	5	6	1	2	3	4	5	6
Start	-5	0	17	0	0	0	2	3	15	-22	-5	-9
+175°F, 24 Hours	1	3	17	45	17	8	2	0	3	-5	7	9
+175°F to -65°F (10 Times)	25	27	-15	25	25	10	3	0	9	-5	14	10
1.4 g's, 35 cps, 4 hr, -65°F	2	-3	32	67	70	15	5	135	62	5	120	108
1.4 g's, 35 cps, 4 hr, +175°F	17	12	5	82	75	30	15	128	76	13	115	100
3 g's, 13 cps, 8 hr, amb.	20	23	145	91	87	34	0	128	65	17	130	100
100% Humidity, 120°F, 48 hr.	-230	230	-197	-228	-106	-140	-10	>-500	-60	112	>-500	

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gages might have shown a shift later which could have been attributed incorrectly to another cause. Therefore, further tests with these four tanks would be inconclusive. Since there was not sufficient time to regage these tanks, the tests were terminated.

### 3. Compound A

The volume of each Compound A tank was also determined with water. The tanks were cleaned and passivated with Compound A vapors and loaded to 6-10% ullage at the maximum storage temperature. As for the fuel, the ullage calculation was based on the tank volume and did not include the pressure gage tube or fittings on top of the tank.

The eight Compound A tanks were stored for 90 days as specified in the test plan. The ultrasonic measurements were taken two times a week with the exception of two periods discussed later. The ultrasonic evaluation included both wall thickness measurements and inside tank surface finish indications.

The majority of the measurements were made by manual application of the 1/2 inch dual element transducer for wall thickness and the 1/4 inch single element transducer for surface finish. Two 1/4 inch dual element ultrasonic transducers (5.0 MHz) were permanently mounted for the three month test period to simulate a remote missile installation. A two component, room temperature vulcanizing silicone rubber (General Electric RTV-560) was used for both a couplant and a bonding agent. One transducer was bonded to tank 15A containing Compound A and the second transducer was attached to a sulfuric acid tank described in the next section.

One of the installations was vibrated before the tank was filled with oxidizer to determine the effect of environmental conditions to be expected in a launch application. The tank was filled with water to a 5% ullage and vibrated for 4 hours at 1.4 g's at 35 cps and for 4 hours at 3 g's and 13 cps. The signal was still satisfactory after the vibrations and was further evaluated for temperature effects during the three month test program.

The results of the ultrasonic monitoring of the wall thickness are plotted in Figures 28 through 35 (pgs 83 through 90) for the four aluminum and four stainless steel tanks. To separate the data points, the initial wall thickness was plotted at an arbitrary location on the vertical scale for each monitoring station and the vertical scale represents the change in thickness from the initial value. Stations 1 and 2 were in the ullage space near the upper weld and were 180 degrees apart. Stations 3 - 6 were one inch up from the tank bottom in the liquid Compound A portion of the tank.

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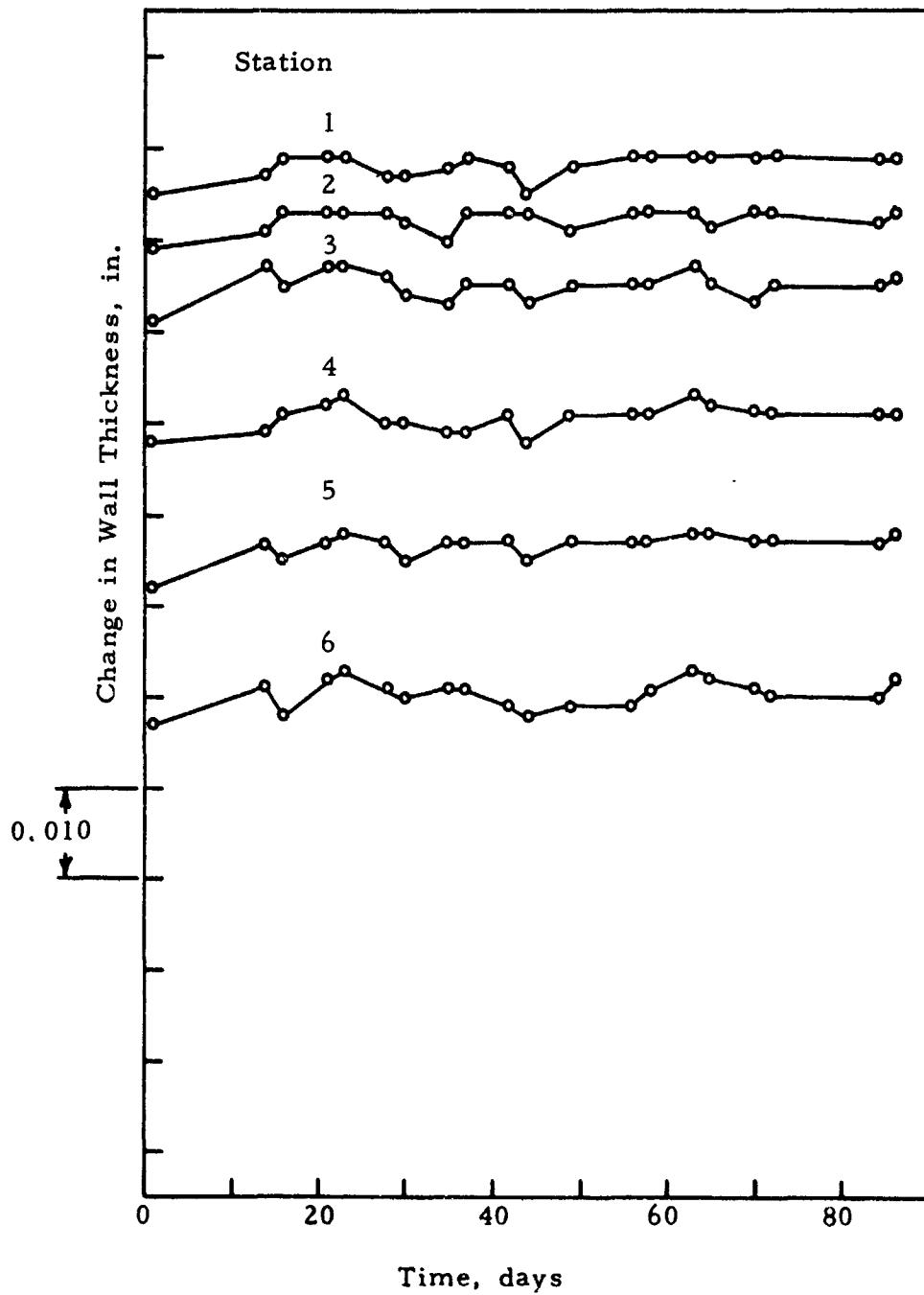
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Figure 28. Wall Thickness History of Tank 13A with Compound A at +175°F

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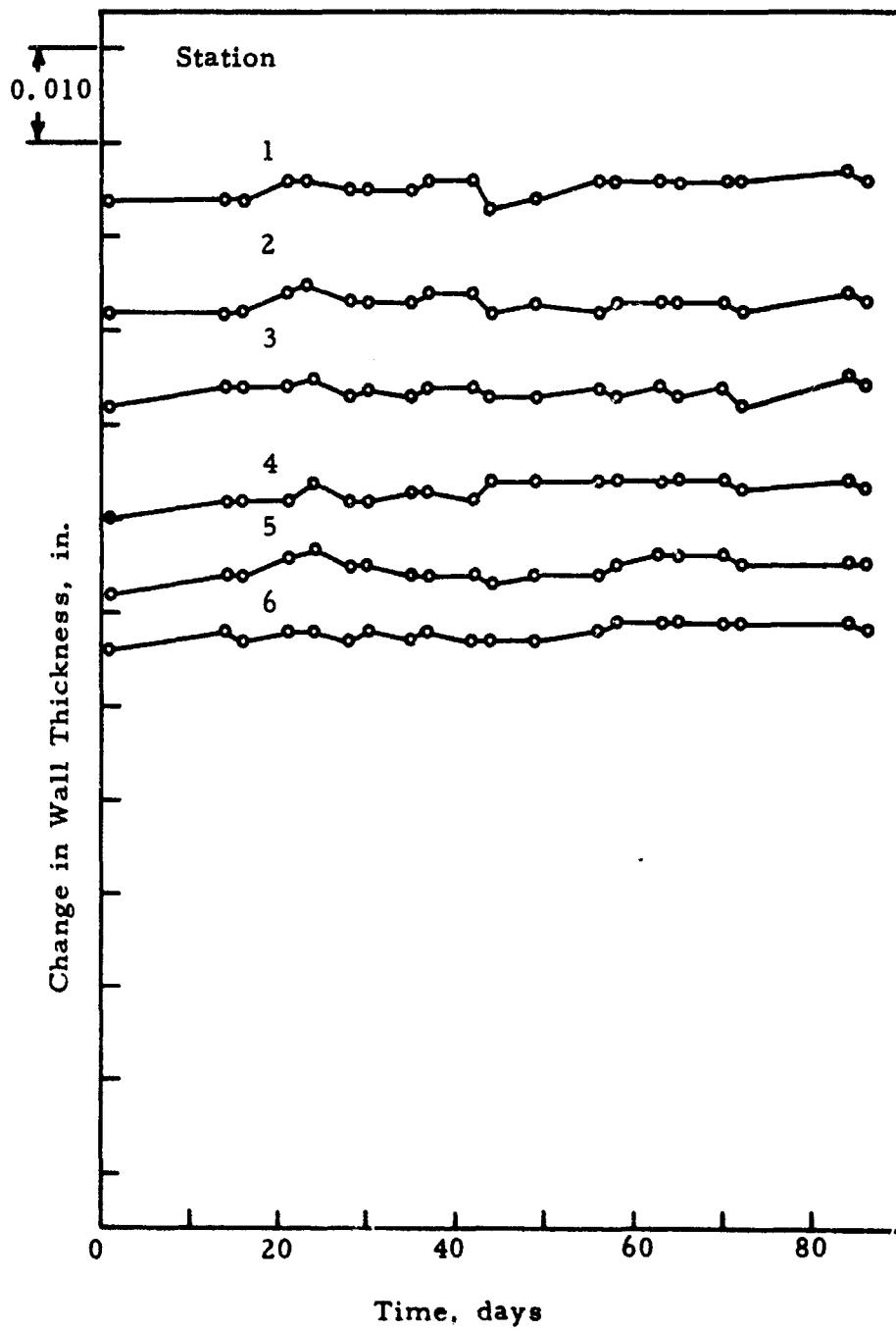
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Figure 29. Wall Thickness History of Tank 14A with Compound A at +175°F

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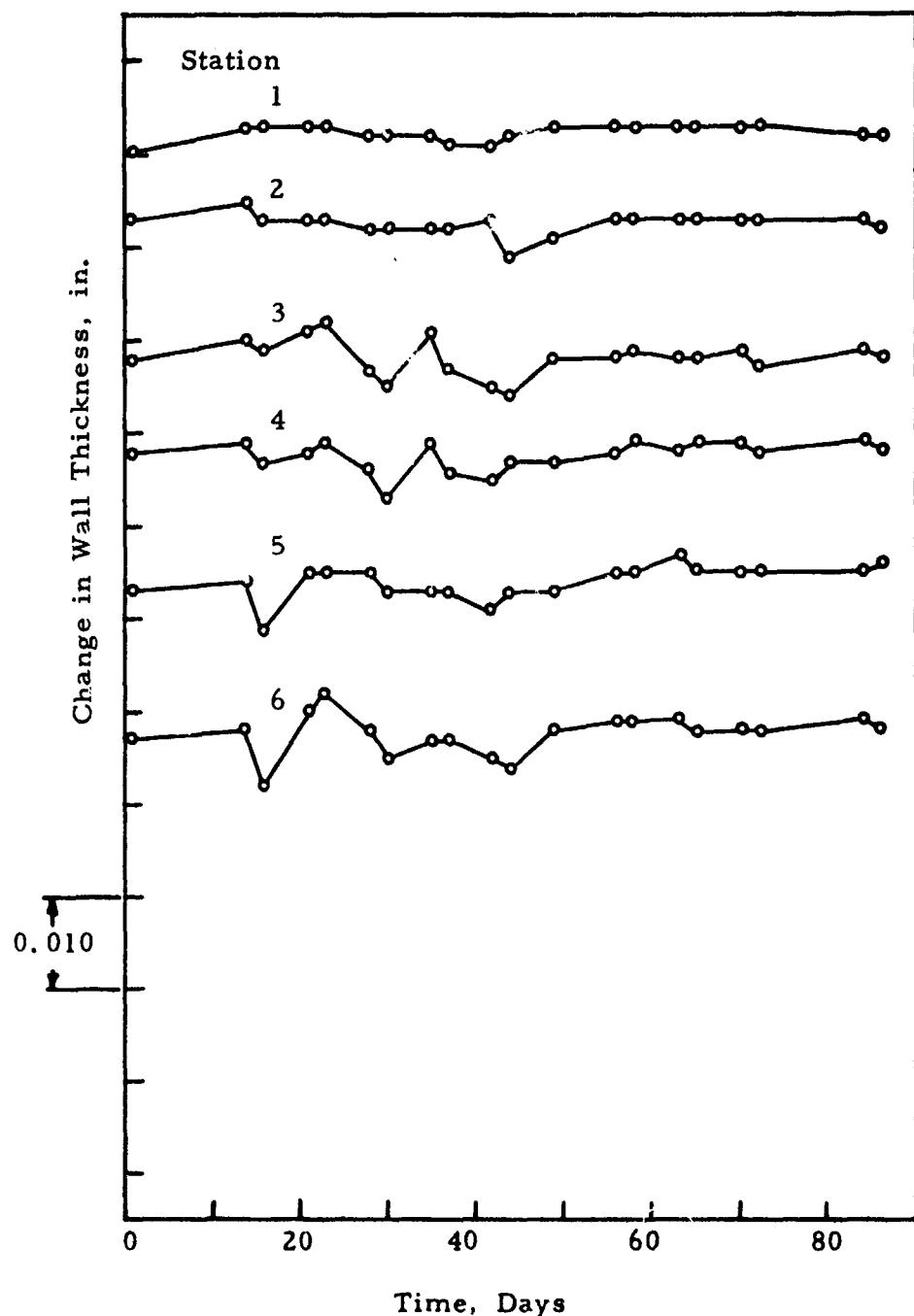
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Figure 30 . Wall Thickness History of Tank 8S with Compound A at +175°F

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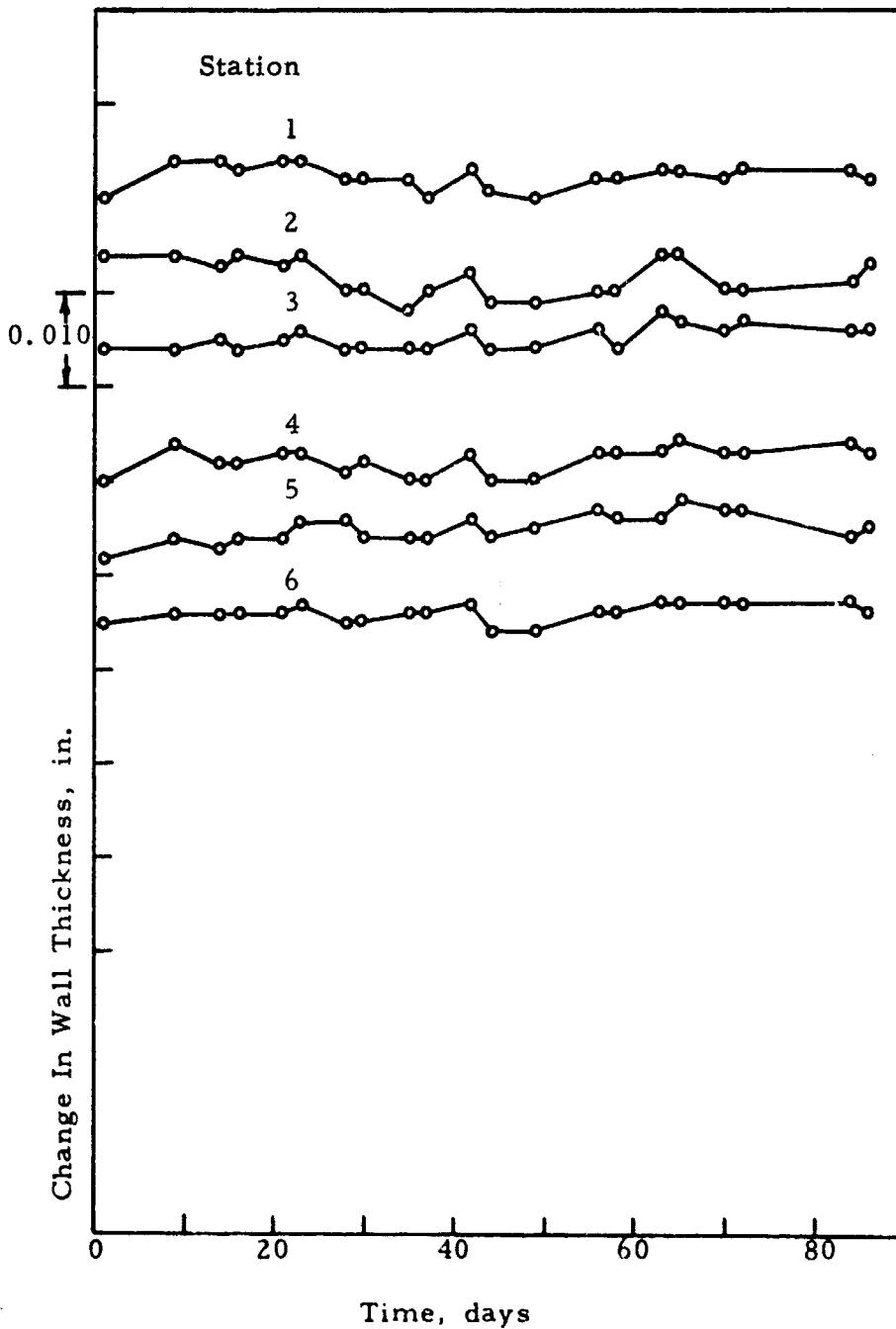
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Figure 31. Wall Thickness History of Tank 12A with Compound A Cycled Between +175°F and -65°F

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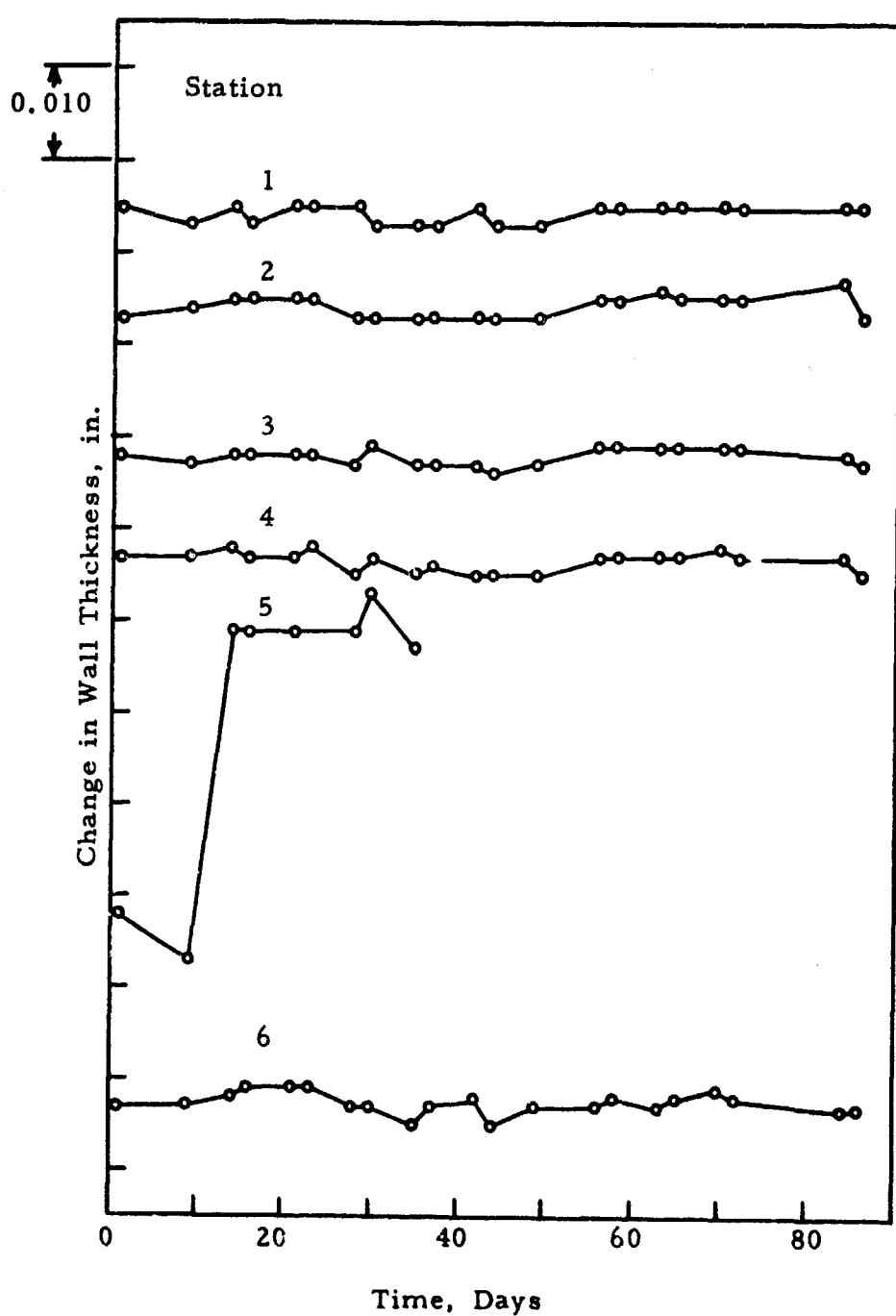
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Figure 32. Wall Thickness History of Tank 15A with Compound A Cycled Between +175°F and -65°F

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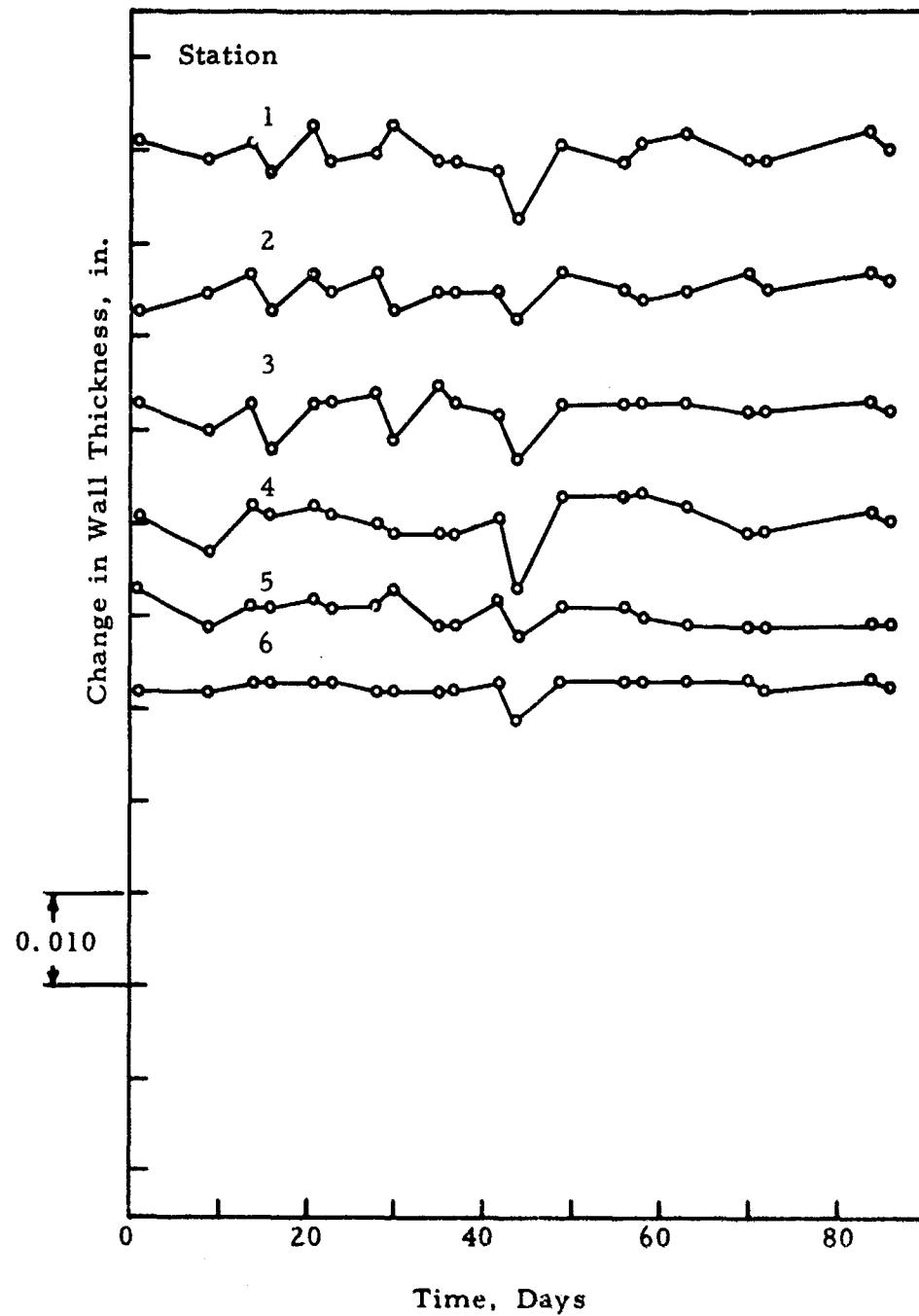
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Figure 33. Wall Thickness History of Tank 9S with Compound A Cycled Between +175°F and -65°F

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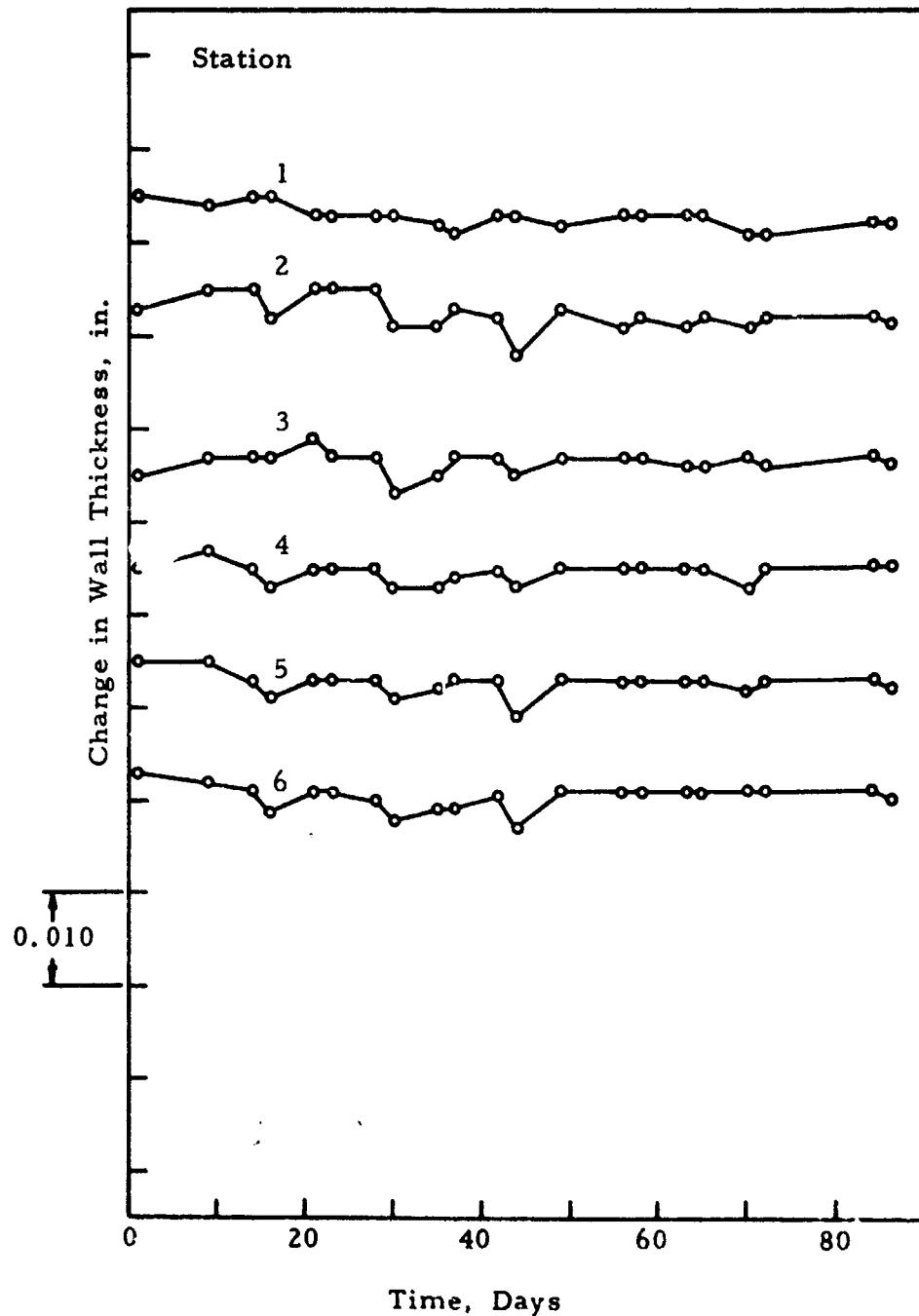
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Figure 34. Wall Thickness History of Tank 10S  
with Compound A at Ambient Temperature

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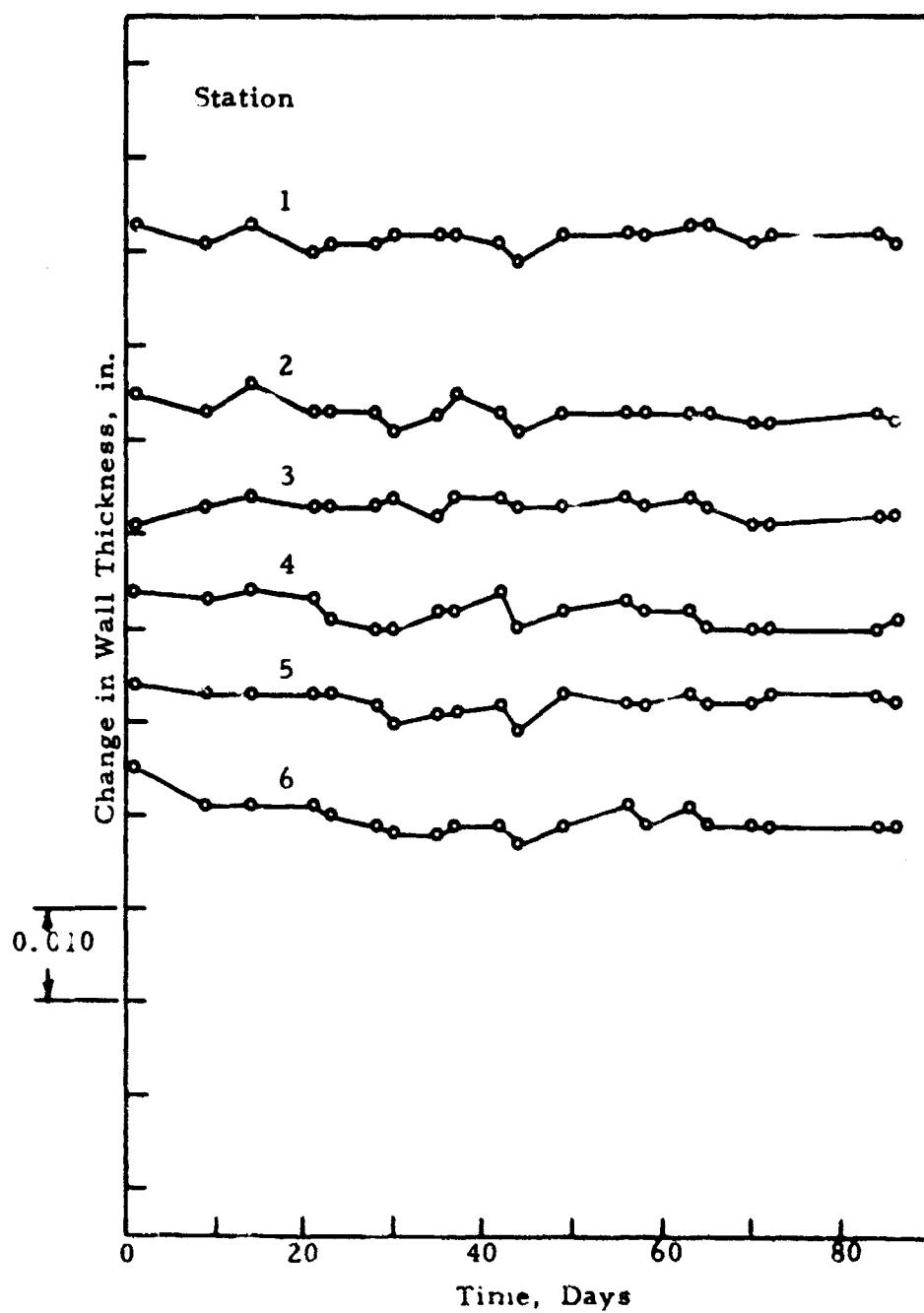
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Figure 35. Wall Thickness History of Tank 11S With Compound A at Ambient Temperature

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Any changes in the wall thickness can be attributed to the accuracy of the instrumentation regardless of the temperature cycle or wall material. From these data, instrumentation accuracy is estimated to be within  $\pm 0.002$  inch. In Figure 32 (pg 87), Station 5 was the transducer mounted with RTV. The transducer indicated an 0.035 inch increase in wall thickness after being heated to +175F. Since the signal strength did not diminish, which would indicate deterioration of the bond, the RTV swelled when heated. The transducer continued to indicate the thicker measurement until day 35 when the signal disappeared indicating loss of bond after a cold cycle.

Attempts were made to measure the wall thickness of the tanks at +175F, but the transducers drifted too rapidly from the heat. The manufacturer has a more expensive transducer with temperature compensation good to 200F. However, for this program, the tanks were allowed to cool for two hours twice a week before taking readings.

Some data points were lost near the end of the test period due to trouble with the digital micrometer. The problem was an erratic loss of readings although the Sonoray unit was functioning properly. After the test period was over, the digital micrometer was returned to the manufacturer for repair and the problem was discovered in the connecting cable between the Sonoray and the micrometer.

The inside surface finish in the Compound A tanks was monitored by noting the attenuators needed on the Sonoray to squelch the multiple reflections from the inner wall. The five attenuators represent 32, 16, 8, 4, and 2 decibels, so readings are some combination of these numbers. Representative readings for each tank are listed in Table XVIII (pg 92).

The reading for Stations 3 - 6 in the liquid portion of the tank are lower than for stations 1 and 2 in the vapor space because some ultrasonic energy is lost into the liquid and less attenuation is needed to squelch the remaining signal. The stainless steel tanks were much rougher than the aluminum from the manufacturing process, since the tubing was not machined on the inside, and no readings could be obtained at the liquid stations. In general, the readings decreased slightly (less attenuation required) over the 90 day test period indicating a slight roughening of the inner surface. Tank 15A showed the most pronounced change at Station 5 which decreased to 0 by day 23. At day 79, the weld at the bottom of the tank showed a small leak near Station 5 as evidenced by a material buildup outside the tank. The leak plugged itself with reaction products, but continued to grow slowly. The tank was sectioned and examined under a microscope. A leak path was visible from the outer surface, through the weld seal, to the inner weld. There was no crack through the inner weld at the sections examined but leakage was established to be due to weld defects from the hand welding operation and not to incompatibility of the material and Compound A. Tank 13A also showed a small leak at the end of the test period, but it was not near any ultrasonic stations.

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**TABLE XVIII**  
**SURFACE FINISH INSIDE TANKS CONTAINING COMPOUND A**

Tank	Day	Attenuator Required to Obtain Zero Signal					
		Station					
		1	2	3	4	5	6
13A	1	16	22	14	14	14	16
	14	24	16	12	16	14	16
	30	24	24	14	14	8	12
	56	12	8	8	10	8	12
	90	12	14	8	8	8	10
14A	1	24	18	16	14	12	14
	16	26	22	10	8	12	12
	30	26	28	6	10	12	14
	56	12	12	8	10	8	8
	90	12	12	6	8	10	6
12A	1	30	18	12	10	14	14
	16	24	30	12	8	10	14
	30	32	22	10	6	8	8
	56	20	20	12	10	10	8
	90	20	18	12	6	6	4
15A	1	26	18	15	14	16	14
	23	28	16	12	10	0	6
	30	20	20	16	10	0	6
	56	16	6	12	8	0	8
	86	18	12	12	8	0	4
8S	1	10	6	0	0	0	0
	14	8	6	0	0	0	0
	28	8	2	0	0	0	0
	56	4	0	0	0	0	0
	90	6	0	0	0	0	0
9S	1	18	20	6	0	0	6
	14	18	22	6	0	0	0
	28	12	12	0	0	0	0
	56	12	8	0	0	0	0
	90	12	8	0	0	0	0
10S	1	6	10	0	0	0	0
	14	12	10	0	0	0	0
	28	6	8	0	0	0	0
	56	4	8	0	0	0	0
	90	4	8	0	0	0	0
11S	1	8	10	0	0	0	0
	14	12	11	0	0	0	0
	28	8	6	0	0	0	0
	56	6	8	0	0	0	0
	90	8	6	0	0	0	0

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A cube of Teflon and stainless steel 5/16 inch on a side were put in tanks 10S and 11S respectively. They were barely detectable with the ultrasonics due to the rough surface finish on the stainless steel. In a missile constructed from smooth sheet, this problem would not exist. No size estimate could be made from the ultrasonics due to the sample being essentially the same size as the transducer.

Sludge measurements were made from the bottom of the tank, but no detectable sludge formed during the test period. This was confirmed when the tanks were cut open after vaporizing the propellants.

The pressure in the tanks at ambient temperature varied from vapor pressure up to 170 psia. The tanks were loaded at about 40F and varying amounts of gaseous nitrogen were introduced in the loading process causing additional pressure above the vapor pressure. The tank pressures were monitored by the visual gages on each tank as a safety precaution and no significant pressure rises occurred.

The Compound A was sampled when the tanks were initially loaded and analyzed as 99.5% Compound A and 0.5% Cl<sub>2</sub> with no other impurities noted. The contents of Tank 15A were analyzed at the end of the test period to be sure foreign material was not present to cause the leak. The analysis was 99.5% Compound A with trace quantities of Cl<sub>2</sub> and HF, indication no propellant degradation.

#### 4. Sulfuric Acid

A total of six 0.25 inch wall aluminum tanks were tested with duplicate samples of 30%, 40% and 50% sulfuric acid to accelerate and vary the corrosion rate. With a faster corrosion rate than anticipated with the Compound A tanks, the acid allowed a better demonstration of the capabilities of the ultrasonic equipment.

The data taken were similar to the measurements for the Compound A tanks. The wall thicknesses as a function of time are plotted in Figures 36 through 41 (pg 94 through 99). Stations 1 and 2 are in the vapor space, Stations 3 - 6 are one inch up from the bottom equally spaced around the tank, and Stations 7 and 8 are the tank bottom which was machined to 0.450 inch thickness.

In the test plan, the tanks were scheduled to be temperature cycled from -65F to +175F. Even at ambient temperature, the gas evolution was so rapid, particularly from the 30% tanks, that the tanks could not be sealed for any period of time and were left vented continuously. One tank of each concentration (7A, 9A and 11A) was heated to +175F on the seventh day, but the vented tanks boiled dry in less than three hours. Therefore, these three tanks were reloaded with fresh acid solutions and were stored at about 75F for the remainder of the test period.

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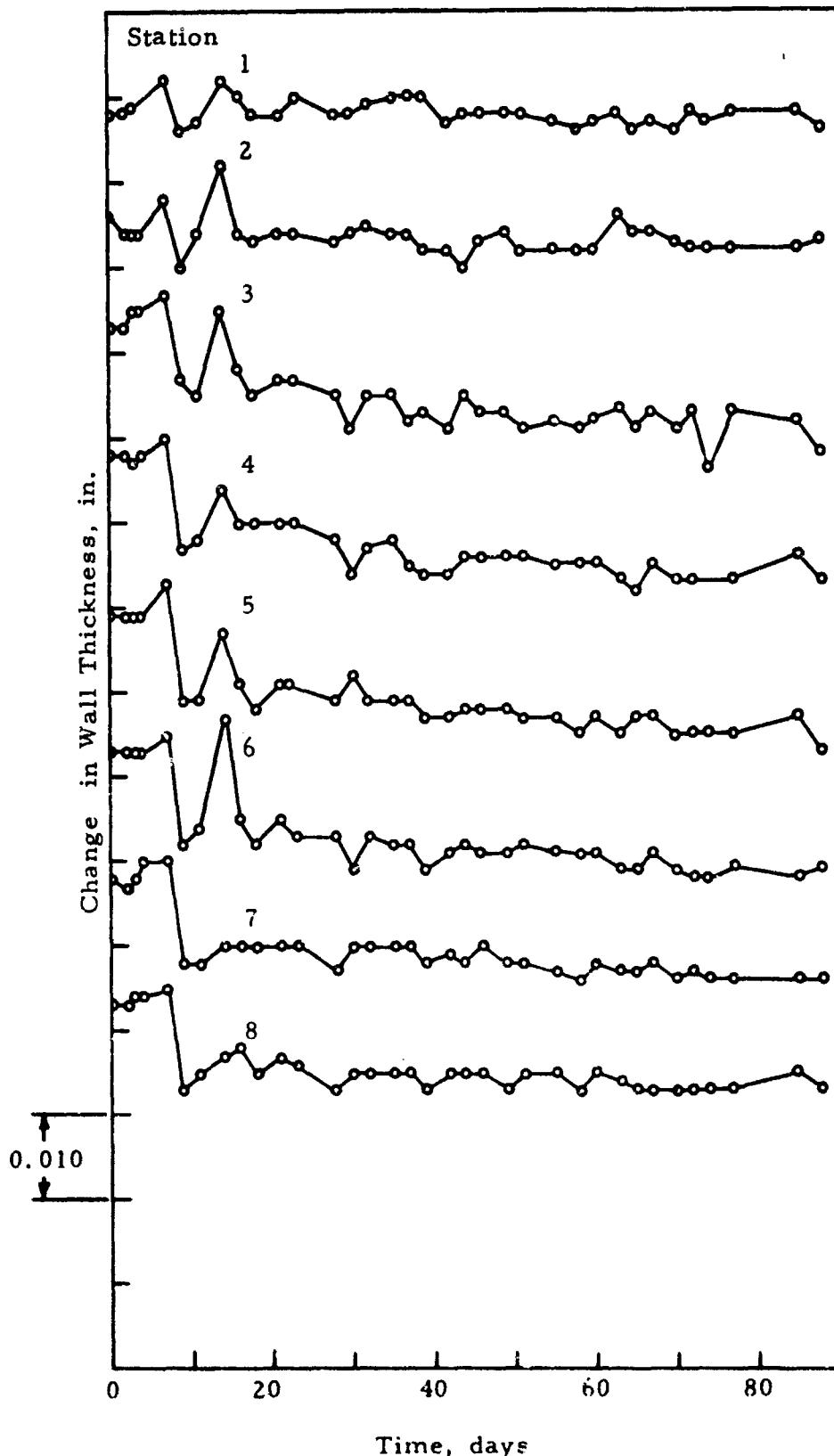


Figure 36. Wall Thickness History of Tank 7A with 50% Sulfuric Acid

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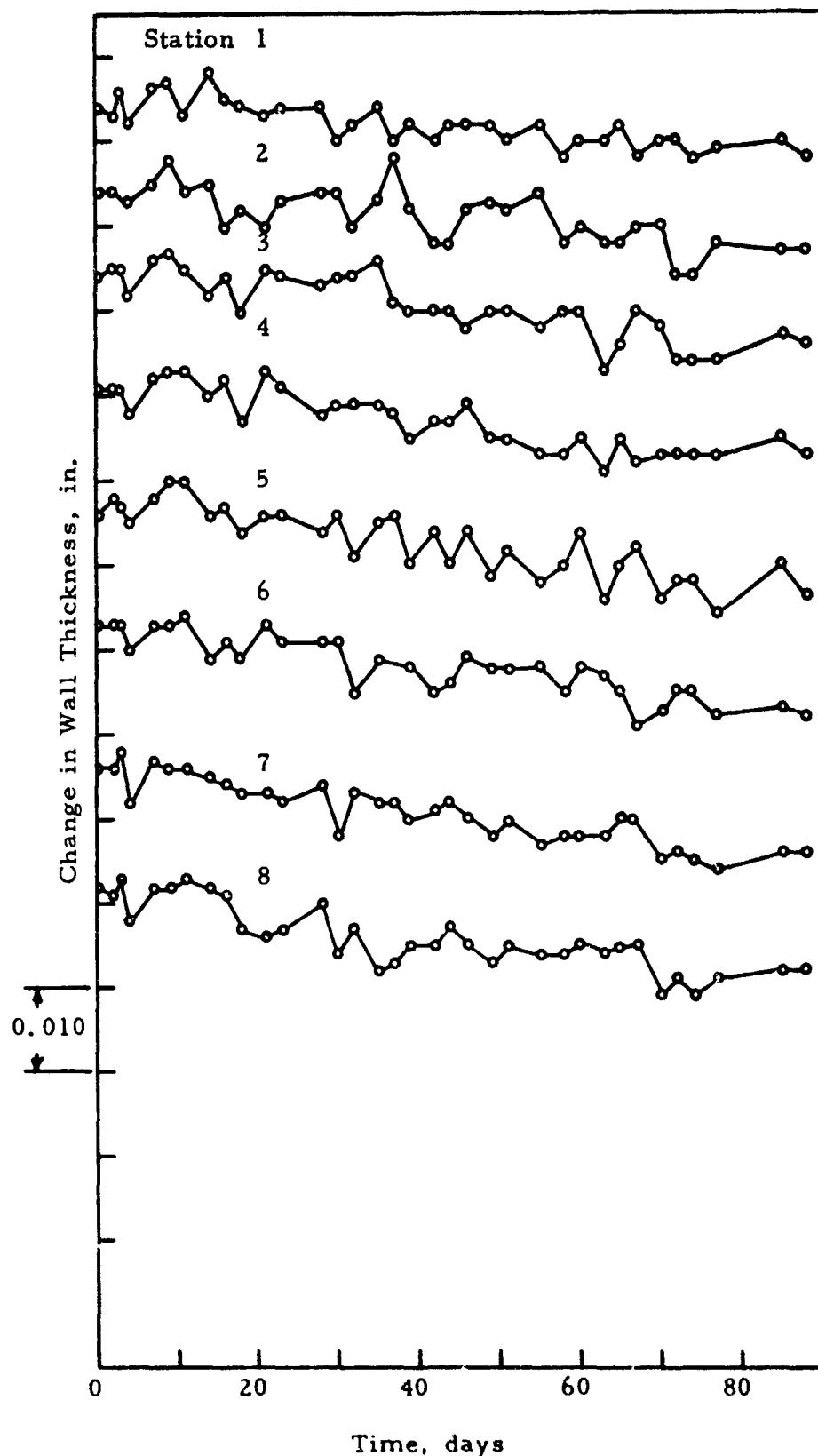


Figure 37. Wall Thickness History of Tank 8A with 50% Sulfuric Acid

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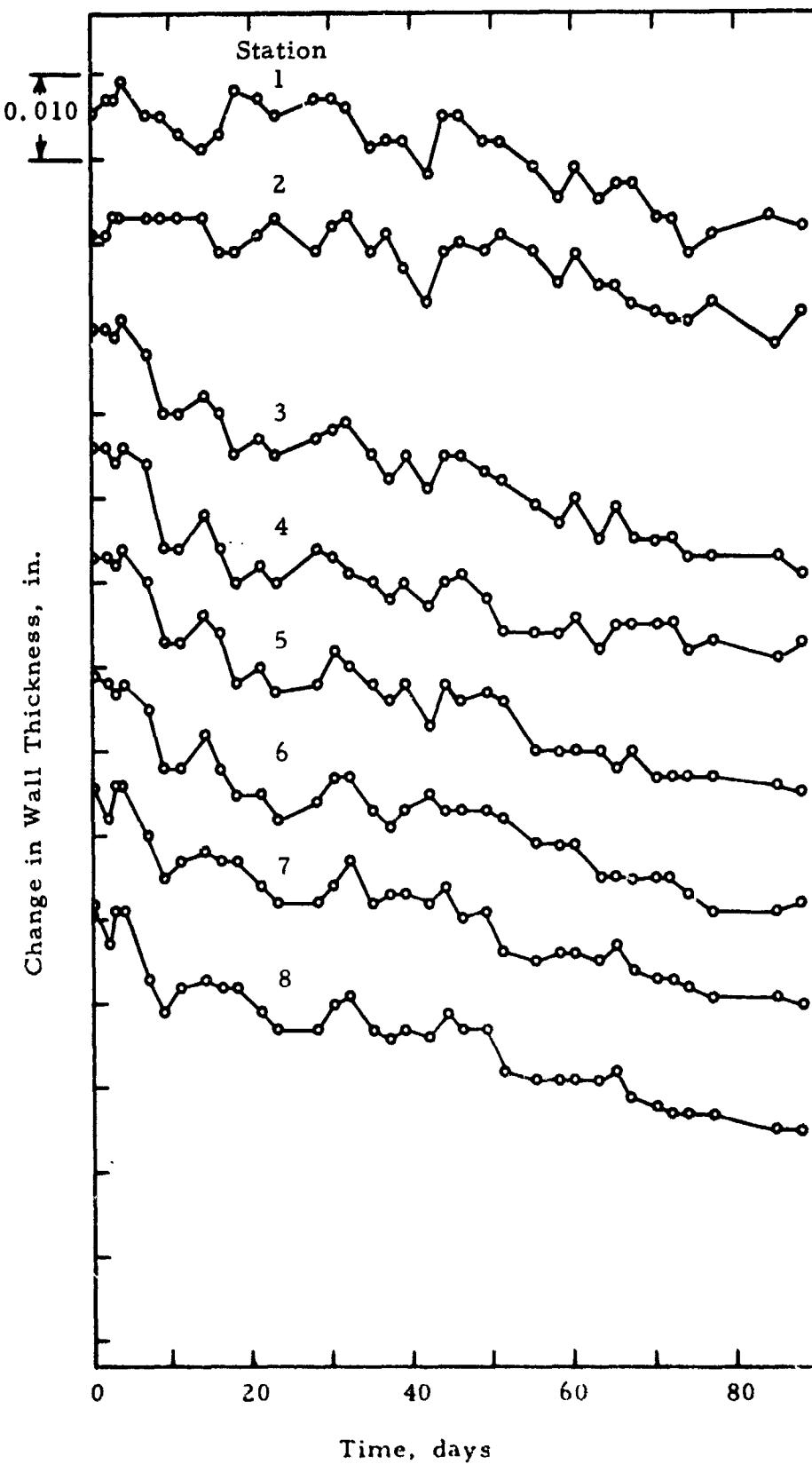


Figure 38. Wall Thickness History of Tank 9A with  
40% Sulfuric Acid

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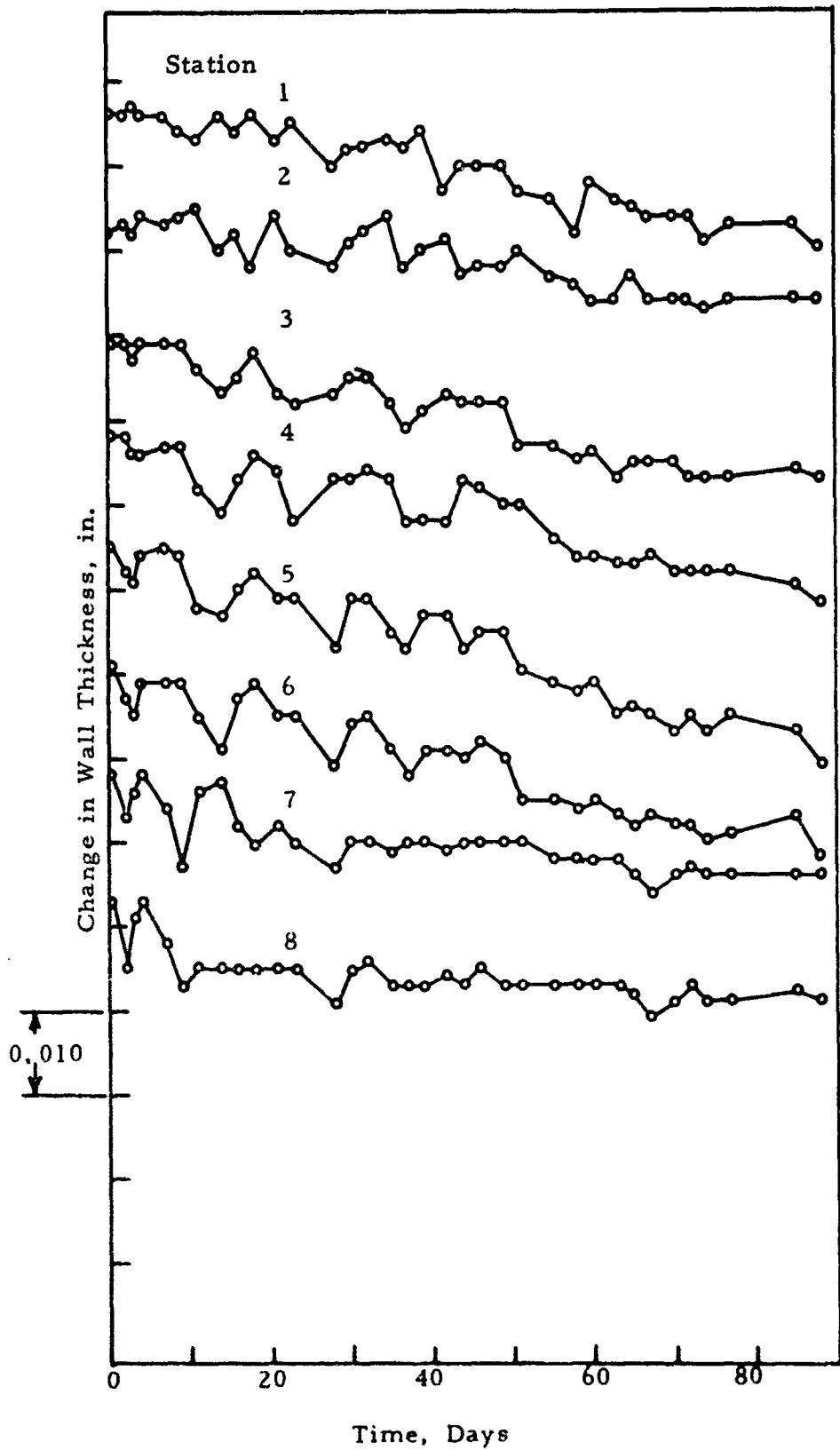


Figure 39. Wall Thickness History of Tank 10A with  
40% Sulfuric Acid

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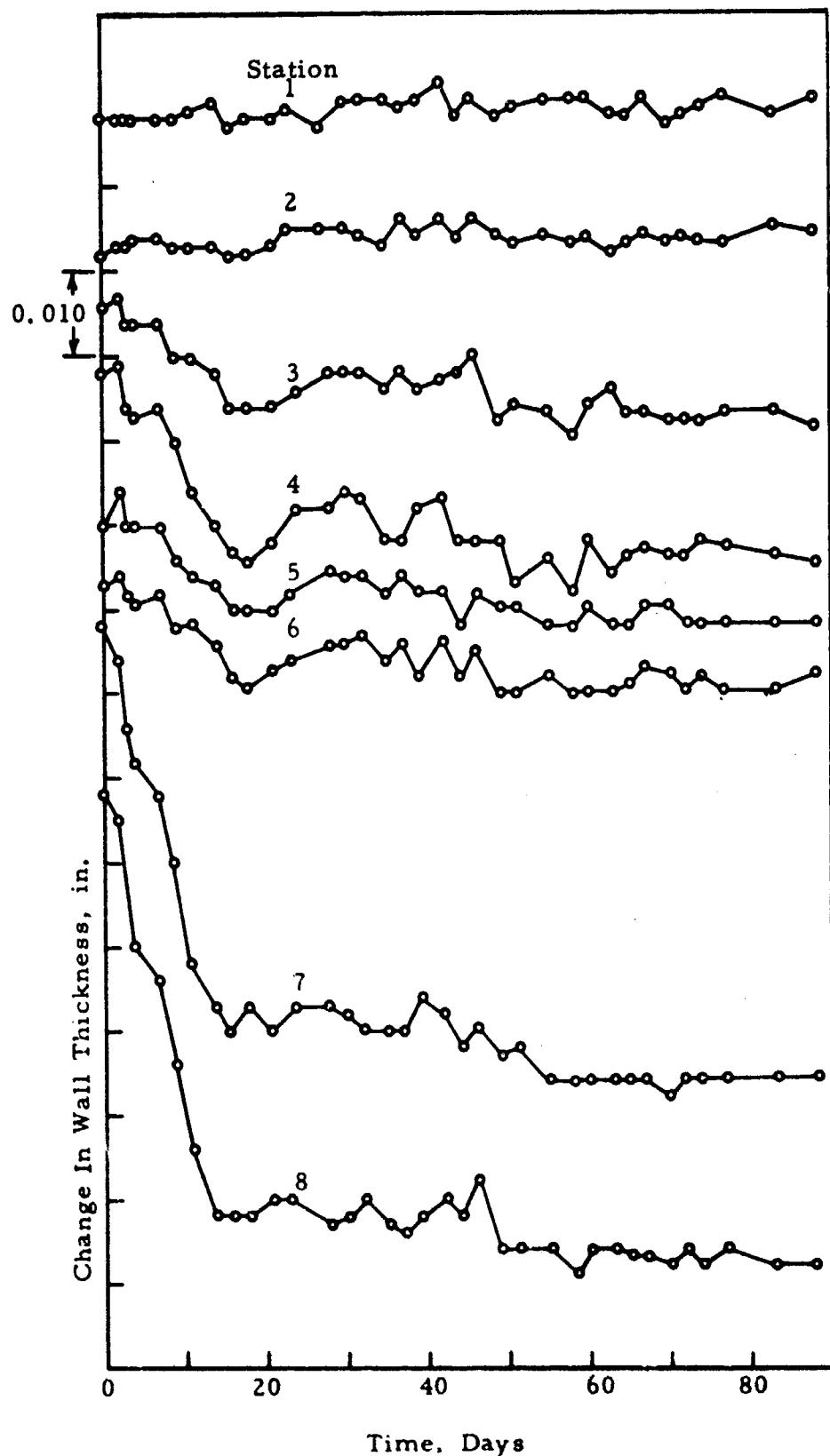


Figure 40. Wall Thickness History of Tank 11A with  
30% Sulfuric Acid

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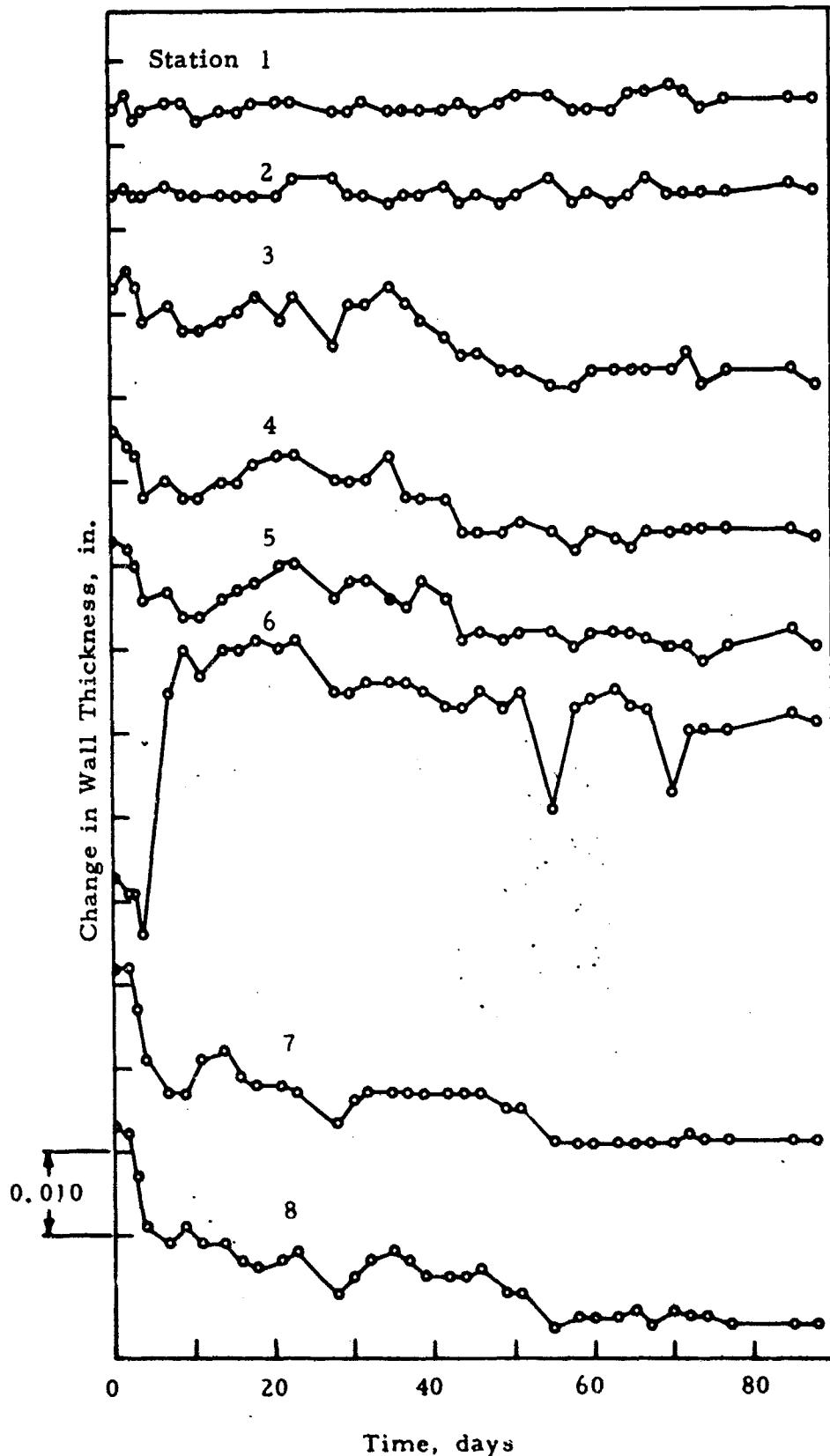


Figure 41. Wall Thickness History of Tank 16A with 30% Sulfuric Acid

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The 50% acid solutions in Figures 36 and 37 (pg 94 and 95) indicated about half as much corrosion in the vapor as liquid areas with about 0.040 inch per year in liquid. The abrupt wall thickness reduction in Figure 35 corresponds to the high temperature test conditions.

The 40% solution in Figures 38 and 39 (pg 96 and 97) was more corrosive with rates of about 0.10 inch per year. Again, the vapor space showed significant thickness reduction, but the bottom of tank 10A was more resistant to corrosion.

The 30% solutions in Figures 40 and 41 (pg 97 and 98) showed no reduction in the vapor space. The bottom plate in tank 11A was severely corroded for the first 15 days. Station 6 on tank 16A was the other transducer attached permanently with RTV. It also showed an increase in wall thickness although the tank was not heated. After the initial swelling, it indicated wall thickness reduction consistent with the other three stations in the liquid portion.

The data scatter for the acid tanks is greater than for the Compound A tanks. This is attributed to the greater corrosion creating uneven surfaces to measure in the acid tanks.

After the 90 days, the tanks were emptied, cut open and mechanical measurements taken at the same stations. Table XIX (pg 101) compares the final ultrasonic thickness measurements with the mechanical measurements. For tanks 11A and 16A, neglecting the permanent transducer on 16A, all but one measurement agree within 0.003 inch or less. Differences up to 0.011 inch are shown for the higher acid concentration tanks which had a much rougher interior surface. In all but one case, the ultrasonic reading is higher. The differences are greater than were anticipated, especially since the larger differences occur in the vapor space. Probably solid material, which tended to plug the fill hole, also formed on the tank wall in the vapor space and gave a false additional wall thickness indication.

When the tanks were emptied, the 40 and 50% tanks were almost completely solid. The acid had reacted with the aluminum to form aluminum sulphate. The 30% acid tank was analyzed at the end of the test period at 14.0% sulfuric acid. The tank reacted with aluminum faster than the water evaporated and the acid solution became weaker as the test progressed.

Surface finish readings were taken for these tanks as well as the Compound A tanks. After a week, the surface of the 30% acid tanks was corroded to the limit of the attenuator switches as shown in Table XX (pg 102). The stronger acid solutions corroded the tank in less than two days.

When the corrosion became severe enough to reduce the surface finish readings to zero, it was no longer possible to get sludge or liquid level readings since a signal cannot be reflected from the far wall through the liquid.

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TABLE XIX  
COMPARISON OF ULTRASONIC AND MECHANICAL THICKNESS MEASUREMENTS

Tank	7A		8A		9A		10A		11A		16A	
	U	M	U	M	U	M	U	M	U	M	U	M
1	0.266	0.257	0.268	0.259	0.247	0.243	0.250	0.243	0.279	0.268	0.265	0.264
2	0.263	0.252	0.257	0.253	0.267	0.259	0.264	0.262	0.264	0.258	0.264	0.263
3	0.253	0.250	0.256	0.250	0.236	0.243	0.241	0.251	0.250	0.256	0.257	
4	0.253	0.250	0.258	0.258	0.250	0.238	0.236	0.249	0.245	0.244	0.253	0.250
5	0.248	0.243	0.256	0.250	0.235	0.234	0.244	0.247	0.248	0.247	0.250	0.249
6	0.254	0.244	0.257	0.251	0.237	0.234	0.243	0.240	0.252	0.250	0.286	0.250
7	0.436	0.430	0.436	0.430	0.420	0.417	0.436	0.430	0.394	0.393	0.426	0.424
8	0.438	0.430	0.437	0.430	0.420	0.418	0.436	0.425	0.392	0.390	0.424	0.425

U = wall thickness, in., as measured by the ultrasonic equipment

M = wall thickness, in., as measured with dial indicator calipers

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**TABLE XX**  
**SURFACE FINISH INSIDE TANKS CONTAINING SULFURIC ACID**

Tank	Day	Attenuator Required to Obtain Zero Signal					
		1	2	3	4	5	6
7A (50%)	0	24	22	14	14	16	12
	2	0	0	0	0	0	0
8A (50%)	0	24	20	14	14	14	14
	2	0	0	0	0	0	0
9A (40%)	0	22	30	16	14	14	12
	2	0	0	2	4	2	4
	3	0	0	0	0	0	0
10A (40%)	0	22	24	12	16	16	14
	2	0	0	2	0	2	4
	3	0	0	0	0	0	2
11A (30%)	0	30	30	14	14	14	12
	2	26	26	6	6	8	10
	3	30	30	2	2	6	6
	4	14	14	0	0	4	6
	7	0	0	0	0	1	9
16A (30%)	0	30	30	12	14	16	16
	2	24	20	6	8	6	6
	3	18	16	2	2	2	2
	4	10	0	4	0	0	0
	7	4	4	6	0	0	0

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Foreign objects were placed in two of the fuel tanks. A 1/4 inch cube of ethylene propylene was placed in 4S and a cube of butyl rubber in 5S before the tanks were loaded with fuel. Probably the ethylene propylene caused the additional pressure rise in tank 4S. The cubes could be detected with the ultrasonic equipment, but due to their small size and the rough surfaces of the stainless steel tanks (compared to the aluminum tanks used for the evaluation tests) the size could not be determined. Therefore, no change in the sample sizes from swelling or degradation could be detected. After the tanks were emptied, there was no trace of the ethylene propylene and the rubber had disintegrated into small pieces of residue.

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VI

**CONCLUSIONS**

Since the results from Phase I and Task I of Phase II determined the direction of the succeeding tasks, they have been summarized in detail at the end of each section describing a block of work. This section includes the more significant results of the preliminary work as well as specific conclusions resulting from the prototype equipment evaluation in Task II of Phase II.

The ultrasonic pulse-echo technique has demonstrated its limited adaptability to monitoring long-term storage of tanks containing corrosive propellants. The ultrasonic equipment used for the feasibility demonstration consisted of general purpose instruments which are more complex than would be required for a specific application, but the ultrasonic principle can be used to develop a very simple go-no-go type of monitor. The simpler design would also eliminate the need for the design compromises of a general purpose instrument and would reduce or eliminate some of the problems encountered in this program.

Ultrasonic equipment can monitor wall thickness and internal surface corrosion in both the liquid and ullage portion of the propellant tank. Improved transducers are being developed commercially which will reduce the minimum wall thickness which a pulse-echo device can measure from 0.050 to 0.030 inch. The accuracy of the wall thickness determination was 0.002 inch under ideal conditions and was only 0.010 inch with heavily corroded curved surfaces. Reading accuracy can be improved by shaping the transducer face to fit the curvature of the tank to eliminate "hunting" for a minimum value of thickness when using a flat-faced transducer. Fixed transducers would eliminate variations in couplant thickness, location and orientation, particularly for a heavily corroded surface. The calibration drift in the existing equipment could also be improved.

With the ultrasonics, the liquid-vapor interface level, sludge buildup and foreign materials can be detected in a propellant tank until the wall corrosion becomes sufficient to scatter the ultrasonic signal excessively. When the corrosion is severe enough to mask the other effects, the propellant system would probably be taken out of service. Wall thickness can still be monitored with the corroded wall.

Although the ultrasonic readout equipment can be redesigned for a five-year life, a better method of transducer attachment must be developed for permanent installations. Either a single couplant and adhesive material or a transducer mounting with confined couplant is needed which will function for at least five years over the temperature range predicted for the particular missile system.

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Foil strain gages have been used to monitor the internal pressure increase in a tank resulting from decomposition of a propellant. Extrapolating the results of the three month test program accomplished on this project, it would appear possible to achieve a five-year life with the strain gages. The errors in strain gage indications during the three months were a combination of random variations due to contact resistance, hysteresis, etc., and a time dependent change due to drift in the strain gage zero balance. The zero balance change appeared to be independent of pressure level and was principally a result of aging. Comparison of initial and final calibrations after three months confirmed that the zero balance, not a calibration change, was responsible for the error which increased with time. Longer test periods are needed to determine if the zero balance continues to change at the same rate and acceptable error limits must be established for a specific installation.

More sophisticated readout devices, which are readily available as commercial items, are desirable for an eventual application to reduce the time for monitoring multiple channels of data. A reduction in the number of connections with their varying contact resistance would reduce the random errors and redundant checks could be incorporated to identify a gage which is indicating a false pressure.

From the calibration data, strain gages may also be installed on tanks already filled with propellant, which prevents calibrating each gage, if wider error limits are permissible. Of course, the gage will indicate pressure increase from the date of installation rather than absolute pressure.

The thermal conductivity cell has demonstrated a good potential as a leak detector for Compound A and MHF-5 under laboratory conditions. Although limited by the available auxiliary equipment, both sensitivity and selectivity were demonstrated. Additional tests, as indicated in Section VII, should be made to determine if the thermal conductivity principle is adaptable to field environmental conditions.

In general, the feasibility of applying NDT techniques to propellant monitoring has been successfully demonstrated. Now these techniques should be further developed for a specific application, as recommended in the next section, to establish the potential utility or readiness condition of a deployed missile.

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## VII

## RECOMMENDATIONS

The non-destructive techniques which were selected for monitoring liquid propellant degradation on this program have proven feasible with Compound A and MHF-5 propellants. Other propellants with degradation modes similar to these two propellants can be monitored by the same NDT techniques. The results of the feasibility demonstration in this report should be directed to a more specific application which would permit simplifying the instrumentation and increasing the accuracy of the indications.

As one example, consider an application using Compound A and a hydrazine-based propellant in tanks with 0.035 inch walls. The tanks will be in an enclosure formed by the missile body and the entire missile will be stored at a remote location. The propellant monitoring must be done remotely and frequently.

The missile enclosure or the area outside the missile could be monitored with the thermal conductivity apparatus. However, additional research is required to identify the requirements and capabilities of a suitable system which would consist of the detector, power supply and indicator. All tests to date have been in a closely controlled nitrogen atmosphere and the technique should be evaluated under more stringent environmental conditions. The inert nitrogen atmosphere should be replaced with air and common contaminants such as CO<sub>2</sub>, smoke and moisture should be introduced to find the effects on system sensitivity and if false alarms are generated. Other filament materials should be evaluated to increase compatibility with the propellants and possibly to increase sensitivity. The effect of both filament and environmental temperatures on the sensitivity of the cell must be evaluated. A simple system for propellant selectivity should be developed based on the results to date. Depending on the configuration of the missile and its storage area, a null balance system of two sets of cells may be needed to cancel atmospheric background variations and insure that only a genuine tank leak will actuate the alarm system.

The preceding work is necessary to establish the design requirements and operational limitations for thermal conductivity probes. The final design should be tailored to the specific missile application to attain maximum reliability for the specified conditions.

Ultrasonic equipment can be developed with is simpler and less expensive than the general purpose items used in this program and, at the same time the accuracy and lower limits of use can be improved. Ultrasonics using fixed transducers designed for a limited thickness range can measure

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thickness of the tank wall to within 0.0001 inch and can detect incipient corrosion inside the tank. The order of magnitude improvement in wall thickness accuracy is based upon the manufacturer's claims and was not verified in this program. For the application hypothesized, the transducer would be permanently attached to the tank wall which could be at least 200 feet from the readout equipment. Wall thickness would be indicated by three digital characters representing the last three of the four decimal places. A meter with a single gain adjustment would indicate the degree of internal surface corrosion. Audible or visual limit signals could be included for either or both functions. The corrosion meter would indicate initial surface pitting which might be insufficient to change the wall thickness. Wall thickness would be used for a more severe attack to determine if the tank can still be considered operational.

It is recommended that both of these techniques be developed, particularly the basic evaluation of the thermal conductivity cell under more severe environmental conditions. In addition, longer term tests are needed with the strain gages under similar conditions to evaluate their long term characteristics.

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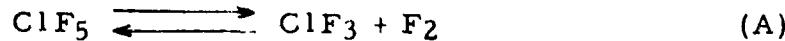
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**APPENDIX A**  
**PROPELLANT SURVEY****A. The Chemistry of Long-Term Storage of Selected Fuels and Oxidizers**

The purpose of this section is to present in some detail the chemical behavior of selected high-energy fuels and oxidizers under long-term storage conditions. The presentation is directed towards use of the information in the development of methods of non-destructive testing of propellants in prepackaged liquid engines, with emphasis on the physical manifestations of the reactions which occur in such environments. Therefore, consideration has been given to both degradation of the propellants and deleterious effects on the container systems, with allowances for possible contamination of the propellant at the time of loading. Specifically, the problems of (1) autodecomposition of propellant; (2) corrosion of tankages; (3) reaction with contaminants; (4) catalysis of autodecomposition by tankages and contaminants; (5) catalysis of wall corrosion by contaminants, have been treated. The assumption has been made, however, that the propellant at the moment of sealing the container is reasonably pure and capable of use to perform the mission, i.e., that massive contamination has not occurred, as the methods to be developed on RMD Project 5808 are directed towards monitoring changes during storage after the system has been sealed. Primary attention has been given to MHF-5 and Compound A; other propellants have been treated in slightly less detail. Tankage materials considered have been limited to the 1000, 2000 and 7000 aluminums, 300 stainless steels and  $\alpha$  and  $\beta$  Titanium.

**B. Compound A**

Compound A is a colorless, water-like liquid in the range -103 to -13C, (1 atm), with a vapor pressure of 63.3 psia at 20C.<sup>(1)</sup> Other physical properties are recorded for convenience in Table A-I (pg 110). No evidence of thermal decomposition in the temperature range -65F to +175F has been detected.<sup>(2,3,4,5,6)</sup> At Thiokol-RMD, three containers fabricated from 347 stainless steel were filled with Compound A so as to yield 2% ullage at +160F; no pressure increase was observed over a 453 day period. Some evidence for an equilibrium dissociation:



above 200F has been reported,<sup>(5)</sup> but conclusive evidence is lacking. Such a dissociation would be undetectable in the range -65F to +175F.

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**UNCLASSIFIED****TABLE A-I. PHYSICAL PROPERTIES OF COMPOUND A**

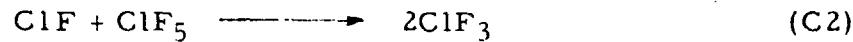
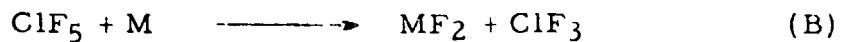
<b>Structural Formula</b>	<b>Classified</b>
<b>Molecular Weight</b>	<b>130.457</b>
<b>Melting Point</b>	<b>-153.4°F</b>
<b>Boiling Point (14.7 psia)</b>	<b>8.4°F</b>
<b>Physical State</b>	<b>Colorless Liquid</b>
<b>Density @ 68°F and 63.3 psia</b>	<b>111.9 lb/ft<sup>3</sup></b>
<b>Viscosity @ 68°F</b>	<b>2.181 x 10<sup>-4</sup> lb/ft-sec.</b>
<b>Vapor Pressure @ 68°F</b>	<b>63.3 psia</b>
<b>Critical Temperature</b>	<b>289°F</b>
<b>Critical Pressure</b>	<b>771 psia</b>
<b>Heat of Vaporization (8.4°F)</b>	<b>37.37 BTU/lb</b>
<b>Heat of Formation @ 77°F</b>	<b>-82.9 BTU/lb</b>
<b>Specific Heat @ 68°F</b>	<b>0.3358 BTU/lb-°F</b>
<b>Thermal Conductivity @ 68°F</b>	<b>0.1252 BTU/ft-hr-°F</b>
<b>Specific Resistance @ 1.4°F</b>	<b>2.22 x 10<sup>9</sup> ohm-cm</b>

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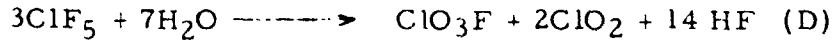
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Compatibility studies with Compound A have been conducted by a number of investigators on a wide variety of aerospace materials. Results of such tests have disqualified titanium tankage for use with Compound A.<sup>(7)</sup> as reaction was visibly apparent at 25C. Results of 30-day compatibility tests expressed in milligrams gained or lost per decimeter squared per day are shown in Table A-II (Pg 112) for aluminums and stainless steels of interest.<sup>(1)</sup> All samples displayed gains in weight except the 2000 series aluminums at ambient temperature and Al 2024 T351 at 150F in contact with vapor. The authors of the referenced report caution that these results are somewhat qualitative and cannot be taken as definitive; the general pattern of fluoride film formation with a gain in weight is in accord with observations of other investigators, however.

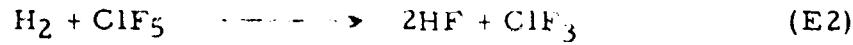
Studies conducted with moisture-contaminated Compound A on these and other metals show a large increase in weight gain over a 30-day period<sup>(1)</sup> The usual fluorination of the metal surface by the interhalogen molecules follows either (B) or (C), depending on the amount of chlorine trifluoride initially present. In either case, fluorination is accompanied by an increase in the ratio of chlorine trifluoride to Compound A in the system. The sheer size of the interhalogens severely inhibits extensive penetration of the fluoride



film once the surface has reacted. With water present, however, the reaction

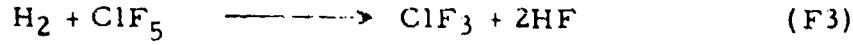


produces a new fluorinating agent, hydrogen fluoride, which can penetrate the surface film with ease relatively speaking. The regeneration of the hydrogen fluoride shown in (E) indicates that the water acts effectively as



a catalyst to accelerate corrosion throughout the storage life of the system.

Similar results can be expected from the inclusion of hydrocarbons in the propellant. The reaction scheme (F) again indicates accelerated



corrosion throughout the storage life of the system. Similar problems can be anticipated with any material which can react with Compound A to generate

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**TABLE A-II. RESULTS OF 30-DAY COMPATIBILITY  
TESTS WITH COMPOUND A**

<u>Sample</u>	<u>Exposure *</u>			
	<u>Liquid, Ambient, T</u>	<u>Liquid, 160°F</u>	<u>Vapor, Ambient, T</u>	<u>Vapor, 160°F</u>
Al 1100	0.063	0.523	0.063	0.650
Al X7002	0.125	0.261	0.125	0.327
Al 7075	0.1205	0.261	---	0.196
Al 7079	0.063	0.392	0.189	0.457
Al 2219	-0.189	0.261	-0.189	0.392
Al 2024T3	-0.189	0.327	-0.189	0.392
Al 2024T351	-0.315	0.261	-0.125	-0.3217
SS 304	0.755	0.261	0.503	0.261
SS 316	0.817	0.327	---	0.196
SS 347	0.880	0.392	0.755	0.457

\* Units shown in Table A-II are milligrams gained or lost per decimeter squared per day.

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hydrogen fluoride. Such a problem is patently not possible should the propellant suffer contamination with oxygen, nitrogen, or helium, commonly-used pressurization gases or "dry-air" contaminants, and, in fact, no acceleration of corrosion is experienced with these contaminants.

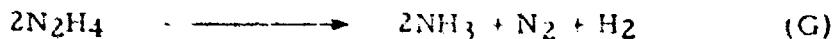
(U) Under ordinary conditions, the fluoride film formed on the metal surface will remain intact. Rough handling, vibrations and/or propellant sloshing may bring about some rupture in the film and possible dislodgement of particles. Such dislodged material may precipitate to form a silt-like sludge. (Metals included from the propellant servicing operation will likewise form a loose sludge of this type, but will not catalyze decomposition or corrosion reactions.) The amount of sludge generated is expected to be minimal in any case; no sludging has been reported by any investigator.

#### C. MHF-5

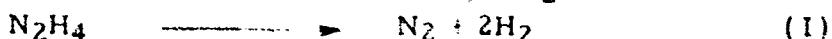
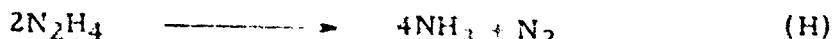
(C) MHF-5 is a liquid in the range -78F to +207F (1 atm.) composed of 55 ± 2% monomethylhydrazine, 26 ± 2% hydrazine and 19 ± 2% hydrazine nitrate, with 2% maximum water and 10 milligrams per liter maximum of particulates. The components are to be MIL-P-27404 MMH, MIL-P-26536B N<sub>2</sub>H<sub>4</sub>, and 98% minimum purity hydrazine nitrate, according to the proposed military specification. Other physical properties are presented in Table A-III (Pg 114) for convenience.

(C) MHF-5 decomposition has been studied at Thiokol-RMD<sup>(8)</sup> under a variety of conditions; these studies are shown in Table A-IV (pg 115). No indications of corrosion of tankage have been detected in any case. The superiority of aluminum tankage over stainless steel is probably due to the well-known<sup>(9)</sup> formation of an impermeable film of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> on the tankage prior to filling. The alumina film is highly resistant to acids and bases under ordinary conditions, and is also so thin that it is largely unaffected by rough handling, vibration and sloshing unless abraded by heavy and rough solid particles. As the film on the tank interior is not exposed to such, the film is not expected to produce sludge by flaking or cracking. No sludges have been observed in storage tanks at Thiokol-RMD.

(C) The decomposition of MHF-5 has been found to produce ammonia, methylamine, nitrogen, hydrogen, and some oxygen. The reaction scheme is apparently very similar to that of hydrazine (G), as might be expected,

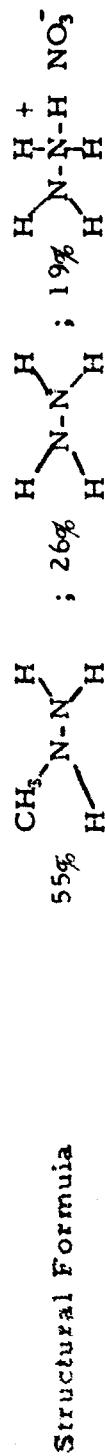


with apparently some decomposition of the nitrate to yield oxygen. Equation (G) is probably a combination of (H) and (I), which represent extremes



of catalytic decomposition under acidic and basic conditions, respectively.

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**CONFIDENTIAL**TABLE A-III. PHYSICAL PROPERTIES OF MHF-5

Molecular Weight (Av)	45.3
Melting Point	-78°F
Boiling Point (14.7 psia)	207°F
Physical State	Colorless liquid
Density @ 77°F and 14.7 psia	60.3 lb / ft <sup>3</sup>
Viscosity @ 77°F	$13.8 \times 10^{-4}$ lb / ft-sec
Vapor Pressure @ 77°F	0.75 psia
Critical Temperature (Calc.)	673°F
Critical Pressure (calc.)	$1411^0$ psia
Heat of Vaporization	361.9 BTU/lb
Heat of Formation @ 77°F	237.8 BTU/lb
Specific Heat @ 77°F (Est.)	0.66 BTU/lb °F
Thermal Conductivity @ 77°F	---
Specific Resistance @ 77°F	---

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TABLE A-IV. THERMAL DECOMPOSITION OF MHF-5

Container Metal	Voltage	Temperature	Time days	Total Pressure Rise psi	Average $\Delta P/t$ for interim
317 Stainless Steel	54	100°F	0-89	204.7	2.3 psi/day
		89-104	255.7	3.4	
		104-181	402.0	1.9	
2014 Aluminum	54	100°F	0-40	8.4	0.21
		40-116	16.8	0.11	
1100 Aluminum*	2%	165°F	0-33	27.4	0.83
		100°F	33-54	36.4	0.43
	54	100°F	54-84	36.4	0.00
		165°F	84-153	115.8	1.15

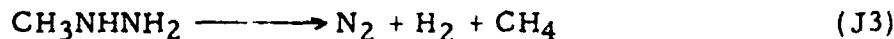
\* 2% voltage @ 165°F = 5% voltage @ 100°F. Samples were cycled.

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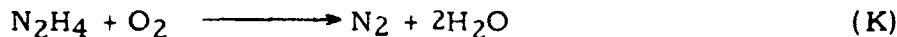
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Equation (H) has also been found to apply for catalytic decomposition of hydrazine on silica, a Lewis acid. The MMH analogs would be (J). No oxidation of the methyl radical has been observed (no CO<sub>2</sub> detected) and no oxides of nitrogen have been detected among the products.



(C) Inclusion of slight amounts of oxygen in the propellant offers no significant problem insofar as performance is concerned; the storability of the system is grossly reduced, however. Assuming the approximate stoichiometry, the degradation of the propellant at completion of the



reaction will be 1.75 percent for a one percent inclusion of oxygen. No catalytic materials are produced in the reaction, which should be complete within a very short period<sup>(10)</sup>. However, in a five percent ullage tank at 100F, the pressure developed would be approximately 4800 psi; the system would obviously be destroyed some time before the reaction would be complete.

(U) A similar calculation can be made for decomposition. Assuming that stoichiometry (H) above were followed (lowest gas evolution per mole fuel consumed), a 1.3 percent decomposition could yield 1000 psi in a five percent ullage system at 100F. Decomposition of the propellant in this situation or oxidation by one percent included oxygen clearly will reduce performance only slightly; the system cannot be considered storable if such pressures are encountered. However, copper, iron, and molybdenum are known catalysts for hydrazine decomposition and thus are to be avoided in favor of aluminum in storage and servicing systems wherever possible. Evidence of unsuitability of stainless steel tankage for MHF-5 was presented in Table A-IV (pg 115). As most welding slags are also known decomposition catalysts for hydrazines, inert-gas welding is recommended for hydrazine tankage.<sup>(11)</sup>

(U) Inclusion of slight amounts of nitrogen or helium in hydrazine propellants is not harmful to the fuels or containers. The same is true of water contamination, provided the water is free of decomposition catalysts such as iron and copper. No deleterious effects on hydrazines have been observed during long-term laboratory storage in containers made of hydrocarbon polymers (e.g., polyethylene), indicating the extent of compatibility of these materials. Some hydrazine is absorbed by the containers but no gross effects are apparent. The containers are usable for long periods of time, do not lose rigidity, and do not exhibit leakage. Silicone lubricants and halocarbons are also suitable for use with hydrazines. Hydro halocarbons (e.g. chloroform, methylene chloride) are not suitable

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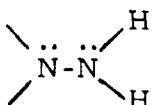
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for use with hydrazines; reaction to yield alkyl hydrazines, hydrohalides and nitrogen occurs readily (11). Reaction between Kel-F grease and hydrazine has also been observed; the products have not been determined, but use of Kel-F grease is not recommended as the reaction impairs its efficiency.

In general, inclusion of slight amounts of ordinarily acceptable greases, oils, sealants and gasketing materials does not offer problems beyond the actual slight reduction in propellant performance which might be experienced with water contamination. The primary storage problem is still that of pressure buildup due to catalytic decomposition of the propellant on the tankage walls.

#### D. Hydrazine Fuels

This section deals with the long-term storage characteristics of the hydrazine fuels listed in Tables A-V-A through A-V-E (pg 118 through 122). Hydrazine becomes more thermally stable as alkylation occurs, hence the approximate order of stability is UDMH > MMH > MHF-3 > Aerozine > Hydrazine. The comparative reaction rates under any given set of circumstances are determined by the electromeric effect of replacing hydrogen by a methyl group. The type of reaction that will occur (as opposed to the rate at which it will occur) is a characteristic of the functional group:

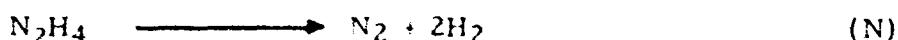


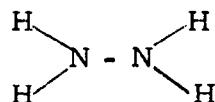
Therefore all hydrazines undergo essentially the same reactions and all are sensitive to the same catalytic agents.

From the point of view of corrosion, all aluminums, stainless steels and titanium alloys are considered highly satisfactory for use as storage container materials. (Spot welded areas are subject to stress-corrosion cracking, however (12)). From the alternate point of view, that of catalysis of fuel decomposition, aluminum alloys are considerably more satisfactory for use with hydrazines than are stainless steels (12, 13). The corrosion resistant nature of aluminum and stainless steel tankage makes pressure buildup due to thermal decomposition the controlling factor in storage of all hydrazine fuel systems. The stoichiometry for catalyzed thermal decomposition of hydrazine(s) is:



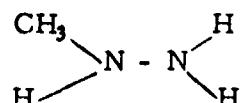
This is probably an equal combination of the stoichiometries under acidic and basic conditions, (M) and (N) respectively.

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**UNCLASSIFIED****TABLE A-V-A. PHYSICAL PROPERTIES OF HYDRAZINE****Structural Formula**

Molecular Weight	32.03
Melting Point	35.6°F
Boiling Point (14.7 psia)	235°F
Physical State	Colorless liquid
Density @ 77°F and 14.7 psia	62.62 lb/ft <sup>3</sup>
Viscosity @ 77°F	$6.08 \times 10^{-4}$ lb/ft-sec
Vapor Pressure @ 77°F	0.27 psia
Critical Temperature	716°F
Critical Pressure	2132 psia
Heat of Vaporization	549.5 BTU/lb
Heat of Formation @ 77°F	675.6 BTU/lb
Specific Heat @ 77°F	0.739 BTU/lb-°F
Thermal Conductivity @ 77°F	---
Specific Resistance @ 77°F	$4 \times 10^5$ ohm-cm
Heat of Fusion	180.2 BTU/lb.

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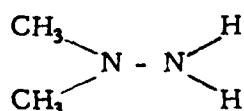
**UNCLASSIFIED****TABLE A - V-B. PHYSICAL PROPERTIES OF MONOMETHYL HYDRAZINE****Structural Formula**

<b>Molecular Weight</b>	46.075
<b>Melting Point</b>	-62.5°F
<b>Boiling Point (14.7 psia)</b>	189.5°F
<b>Physical State</b>	Colorless liquid
<b>Density @ 77°F and 14.7 psia</b>	54.5 lb/ft <sup>3</sup>
<b>Viscosity @ 77°F</b>	$5.1 \times 10^{-4}$ lb/ft-sec
<b>Vapor Pressure @ 77°F</b>	1.0 psia
<b>Critical Temperature</b>	609°F
<b>Critical Pressure</b>	1194.8 psia
<b>Heat of Vaporization</b>	377.3 BTU/lb
<b>Heat of Formation @ 77°F</b>	496.6 BTU/lb
<b>Specific Heat @ 77°F</b>	0.6995 BTU/lb-°F
<b>Thermal Conductivity @ 77°F</b>	---
<b>Specific Resistance @ 77°F</b>	---

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**TABLE A-V-C. PHYSICAL PROPERTIES OF UNSYMMETRICAL DIMETHYL HYDRAZINE**

**Structural Formula****Molecular Weight**

60.09

**Melting Point**

-71.29°F

**Boiling Point (14.7 psia)**

146°F

**Physical State**

Colorless liquid

**Density @ 77°F and 14.7 psia**45.78 lb/ft<sup>3</sup>**Viscosity @ 77°F (extrapolated)** $1.87 \times 10^{-4}$  lb/ft-sec**Vapor Pressure @ 77°F**

25.05 psia

**Critical Temperature**

482°F

**Critical Pressure**

786.5 psia

**Heat of Vaporization @ 77°F**

251 BTU/lb

**Heat of Formation @ 77°F**

382 BTU/lb

**Specific Heat @ 77°F**

0.653 BTU/lb-°F

**Thermal Conductivity @ 77°F**

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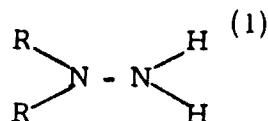
**Specific Resistance @ 77°F**

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**TABLE A-V-D. PHYSICAL PROPERTIES OF AEROZINE-50****Structural Formula**

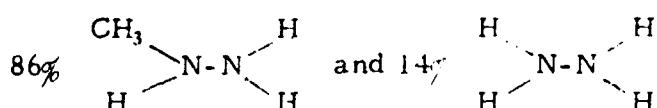
<b>Molecular Weight (Av.)</b>	45.0
<b>Melting Point</b>	18.8°F
<b>Boiling Points:</b> <sup>(2)</sup>	159°F
<b>Physical State</b>	Colorless liquid
<b>Density @ 77°F and 14.7 psia</b>	56.1 lbs/ft <sup>3</sup>
<b>Viscosity @ 77°F</b>	$5.49 \times 10^{-4}$ lb/ft-sec.
<b>Vapor Pressure @ 77°F</b>	2.75 psia
<b>Critical Temperature (Calc)</b>	634°F
<b>Critical Pressure (Calc)</b>	1696 psia
<b>Heat of Vaporization (Calc)</b>	425.8 BTU/lb
<b>Heat of Formation @ 77°F (Calc)</b>	-527.6 BTU/lb
<b>Specific Heat @ 77°F (Calc)</b>	0.694 BTU/lb-°F
<b>Thermal Conductivity @ 77°F (Calc)</b>	0.111 BTU/ft-hr-°F
<b>Specific Resistance @ 77°F</b>	142-161 ohm-cm

(1) R = CH<sub>3</sub> or H; Aerozine-50 = 51% N<sub>2</sub>H<sub>4</sub>, 47% UDMH, 1.8% max H<sub>2</sub>O

(2) Aerozine-50 is not a constant-boiling mixture

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**CONFIDENTIAL****TABLE A-V-E. PHYSICAL PROPERTIES OF MHF-3****Structural Formula**

<b>Molecular Weight (Av.)</b>	43.2
<b>Melting Point</b>	-65°F
<b>Boiling Point (14.7 psia)</b>	194°F
<b>Physical State</b>	Colorless liquid
<b>Density @ 77°F and 14.7 psia</b>	55.75 lb/ft <sup>3</sup>
<b>Viscosity @ 77°F</b>	$3.65 \times 10^{-4}$ lb/ft-sec
<b>Vapor Pressure @ 77°F</b>	1.0 psia
<b>Critical Temperature</b>	617°F
<b>Critical Pressure</b>	1375 psia
<b>Heat of Vaporization</b>	367 BTU/lb
<b>Heat of Formation @ 77°F</b>	535.5 BTU/lb
<b>Specific Heat @ 77°F</b>	0.709 BTU/lb-°F
<b>Thermal Conductivity @ 77°F</b>	---
<b>Specific Resistance @ 77°F</b>	---

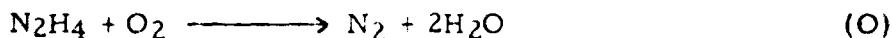
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Selecting (M) as the stoichiometry predicting the minimum amount of gas evolved per mole of propellant decomposed, a quick calculation shows that decomposition of only 1.3% of the fuel at 100F in a 5% ullage system will produce 1000 psi pressure. The loss of 1.3% of the fuel would not affect performance noticeably (especially as it is partially replaced with NH<sub>3</sub> or organic amines) but the tank would be in great danger of rupture. The gas evolution rate of MHF-3 under conditions which simulate metal tankage storage has been presented in Table A-VI(pg 124) as typical of hydrazine fuels in general.

Inclusion of moisture in hydrazine generally does not change the nature or rate of reactions unless the water contains metallic ions which are known catalysts for hydrazine decomposition and oxidation. Inclusion of particles (or ions) of iron, copper or molybdenum, among others, will assuredly accelerate the rate of self decomposition. Inclusion of atmospheric oxygen will result in oxidation of the fuel, especially in presence of iron or copper. Calculations based on the general stoichiometry (O) below show that inclusion of 1% oxygen in a 5% ullage system at 100F will



bring about 1.7% oxidation of the fuel, not enough to seriously affect the performance. The pressure rise at completion would be 4800 psi, however; obviously oxygen inclusion cannot be tolerated for most cases. In all these considerations, generation of pressure is the primary manifestation of reaction.

Non-metals do follow a general pattern in behavior towards hydrazines, but specific products depend on the specific non-metal. Materials containing polar groups are reactive towards hydrazines, whereas non-polar materials are relatively inert. Thus silicones, pvc resins, polycarbonates, polyesters, polyaldehydes, epoxies, polyamides, etc., are reactive with hydrazines; polyethylene, polypropylene, Teflons, etc., are inert. Polyolefins also generally exhibit some reactivity with hydrazines. These materials are used as sealants, gaskets, liners, coatings, etc., and if reactive, will be in danger of mechanical failure long before pressure rises or other physical phenomena are observed or sufficient propellant has been consumed to abort the mission. Should slight inclusion of such materials occur during servicing, no catalytic agents would be produced in the fuel. The net result would be essentially similar to slight inclusion of water.

Inclusion of helium or nitrogen in hydrazine fuels makes no significant difference in storage life of the system.

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**TABLE A - VI. EXTRAPOLATED GAS EVOLUTION RATE OF MHF-3  
AT 160°F AT 5% ULLAGE AND AN S/V OF 0.21 (REF. 13)**

<u>Sample</u>	<u>Gas Evolution Rate</u> <u>(mm-Hg/day)</u>	<u>(psi/day)</u>	<u>Pressure Buildup after 2 yr. Storage (psi)</u>
Al 2014	4.0	0.079	58
Al 7178	3.4	0.066	48
AM 355	9.7	0.188	137
AM355, Fusion Welded	13.5	0.261	191
AM301, M34045	3.8	0.074	54
Ti Alloy	2.0	0.039	28
AFC-77	1.3	0.025	18
AM357	7.2	0.139	101
18% Ni M.S.*	145.1	2.807	2049
	65.4	1.265	923

-----  
\*Maraging Steel

MHF-3 was stored for 390 days at 160°F and 5 percent ullage in Al 2024 (1 liter) containers. The total pressure buildup during this period was 26 psi.

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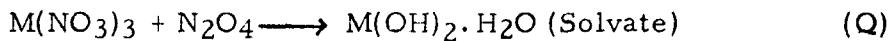
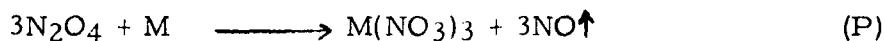
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(C) A feature of hydrazine mixtures (Aerozine-50, MHF-3, MHF-5) worthy of note here is that they will separate to some extent if cycled through the freezing point unless the normal composition of the fuel corresponds to that of the eutectic for the system. Aerozine-50 has been observed to separate somewhat on freezing and thawing<sup>(12)</sup>; such behavior has not been observed for MHF-3 and MHF-5. No studies of the phase relationships of the MMH-N<sub>2</sub>H<sub>4</sub>-H<sub>2</sub>O or MMH-N<sub>2</sub>H<sub>4</sub>-H<sub>2</sub>O-HNO<sub>3</sub> systems have been made as such, however, and it is impossible at this point to predict the separation characteristics of any of these mixtures.

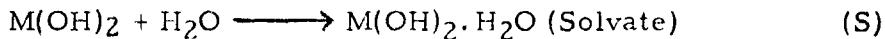
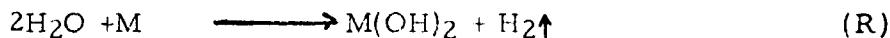
#### E. Nitrogen Tetroxide

(U) Nitrogen Tetroxide is a yellowish to reddish brown liquid between 11.84F and 70.07F (1 atm); other physical properties are listed for convenience in Table A-VII (pg 126). Although N<sub>2</sub>O<sub>4</sub> dissociates to NO<sub>2</sub>, the reaction is reversible and equilibrium values for the dissociation are known within the range -65F to +175F<sup>(12)</sup>. No decomposition of NTO has ever been reported, other than this monomer-dimer equilibrium.

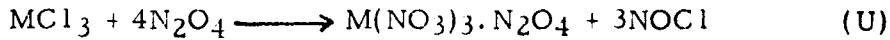
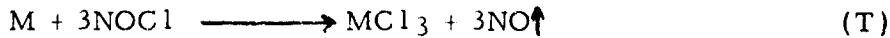
(U) Pure nitrogen tetroxide can corrode metals by a direct oxidation and solvation reaction, producing NO<sup>(14)</sup> (P, Q). These reactions are analogs



of the displacement of hydrogen from water by active metals (R, S). Since NTO is only very slightly ionized<sup>(15)</sup>, however, the reaction is so slow as



to be negligible. In the presence of NOCl, however, the reaction becomes quite rapid. The NOCl in NTO is analogous to HCl in H<sub>2</sub>O and acts as a regenerated catalyst<sup>(16)</sup>:

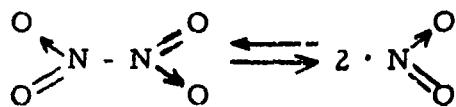


Precautions must be taken to prevent contamination of NTO by chlorine, as most NTO has some free NO in solution. The NO can react with chlorine to produce NOCl, bringing about accelerated corrosion of the tanks.

(U) Contamination of the NTO with water, either from the air or as residue from hydrotesting, yields concentrated nitric acid. The oxidation of metals by concentrated nitric acid is a long-established phenomenon<sup>(17)</sup>.

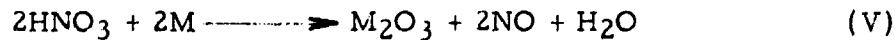
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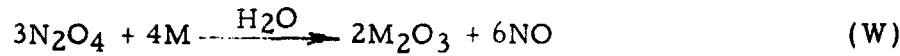
**TABLE A-VII. PHYSICAL PROPERTIES OF NITROGEN TETROXIDE****Structural Formula**

<b>Molecular Weight</b>	92.016
<b>Melting Point</b>	11.84° F
<b>Boiling Point (14.7 psia)</b>	70.07° F
<b>Physical State</b>	Reaish-Brown liquid
<b>Density @ 77° F and 180 psia</b>	89.34 lb/ft <sup>3</sup>
<b>Viscosity @ 77° F</b>	$2.796 \times 10^{-4}$ lb/ft. sec.
<b>Vapor Pressure @ 77° F</b>	17.7 psia
<b>Critical Temperature</b>	316.8° F
<b>Critical Pressure</b>	1469 psia
<b>Heat of Vaporization (equil. mix. @ 70° F)</b>	178 BTU/lb
<b>Heat of Formation @ 77° F (calc. for equil. mix.)</b>	-87.62 BTU/lb
<b>Specific Heat @ 77° F</b>	0.374 BTU/lb-deg F.
<b>Thermal Conductivity @ 77° F</b>	0.0755 BTU/ft-hr-°F
<b>Specific Resistance @ 0° F</b>	---
<b>Heat of Fusion</b>	68.4 BTU/lb

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The overall reaction written for water-contaminated NTO is:



It is important to note that the water is merely a catalyst and is not consumed in the reaction, which can therefore continue unabated unless the oxide coating formed on the surface is impermeable. Many aluminums, stainless steels and titanium alloys form such coatings. Certain materials are also susceptible to corrosion in areas which have been heat-treated due to the precipitation of intermetallic compounds from the alloy along or near weld seams. These intermetallic compounds (e.g. CuAl<sub>2</sub> in Al 2014) are cathodic with respect to the copper-impoverished areas nearby, rendering these areas corrosion-prone, especially to materials of polar character.<sup>(17, 18)</sup> Aluminums of the 1000, 2000 and 7000 series, 300 series stainless steels, and titanium alloys exhibit corrosion rates below 1 mpy to 80F (Table A-VIII - pg 128).

Metal impurities included from servicing systems do not affect the reaction of NTO with tankage, but will ordinarily settle from the liquid unless soluble. As NTO does not decompose, no catalytic effects are to be expected. The gradual reaction of NTO with the metallic inclusions will produce gaseous NO; the size and type of the settled material will not undergo any change, however.

NTO reacts with a large variety of non-metals, especially organic materials. Fluorocarbons and chlorofluorocarbons are generally compatible with NTO.<sup>(12, 19)</sup> Hydrocarbons can be oxidized to yield water and other products; the other products may solvate or settle, but the water produced can accelerate the corrosion of the tankage as discussed above. With the exception of water, products of such reactions are not deleterious to the system during storage unless the original contamination was so great as to materially affect system performance independent of reaction.

Inclusion of oxygen, nitrogen or helium in the propellant is not deleterious to the system.

The most impressive physical manifestation of reaction in the NTO system is the development of pressure. In aluminum tankage at 100F, for instance, a 1-mil reduction of the walls of a spherical 1 liter container will generate 2750 psi, uncorrected for solubility of NO in NTO or for non-ideality of NO. The effects of non-uniformities in tankage composition are so extreme, however, that much greater penetration can occur at several points, especially if some water remains in the microstructure after hydrotesting. Therefore, measurement of pressure generated is not entirely satisfactory as a measure of system dependability. High pressures constitute a warning of lessened dependability but low pressures are not a guarantee of operability of the system. Additional techniques must be employed to determine local stress-corrosion points and the extent of damage at such points.

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**TABLE A-VIII. MATERIALS WITH CORROSION RATES BELOW ONE MPY - NTO  
(ESTABLISHED TEMPERATURE LIMITS)**

<u>Material</u>	<u>Water &lt;0.1%</u>	<u>Water &gt;0.1%</u>
Aluminum 1060	80°F	80°F
	1100	80
	2024	140
Stainless Steel	303	80
	304	140
347	130	130

Titanium alloys are virtually unaffected by NTO.

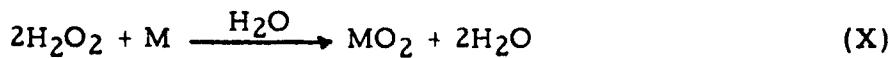
(Ref. 12)

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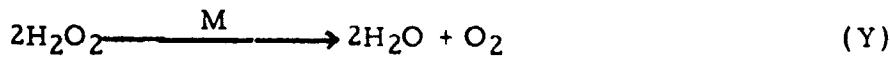
**UNCLASSIFIED****F. Concentrated Hydrogen Peroxide**

Hydrogen peroxide is a colorless, waterlike liquid between -0.43F and +150.2F; other physical properties are listed for convenience in Table A-IX (pg 130). Propellant grade hydrogen peroxide is generally either 90% or 98% in aqueous solution, an important consideration as most hydrogen peroxide reactions involve water as a catalyst. As a matter of fact, the more concentrated forms of hydrogen peroxide exhibit greater stability than the dilute forms, and the decomposition reaction is self-accelerating as water is among the products.(20)

Hydrogen peroxide can attack metals to produce the oxides, as in (X).



Aluminums and stainless steels are generally passivated by this reaction, and further corrosion after formation of an oxide film is not observed. The decomposition of the peroxide (Y) is catalyzed by metal surfaces and ions, however, and the extent of such catalysis becomes the limiting factor

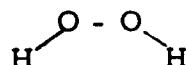


in choosing materials suitable for storage containers. Metals such as iron and copper are highly effective catalysts, limiting the use of stainless steels and copper-bearing aluminum alloys. Reportedly the best container material is pure aluminum, free of surface flaws and weld slags, pre-treated with nitric acid, washed and prepassivated with dilute (30%) hydrogen peroxide. The effects of 90% and 98% peroxide on a variety of aluminums and stainless steels, as well as the resultant stabilities of the peroxide solutions, have been investigated by FMC. Results of these tests are included here as Tables A-X-A (pg 131, 132) and A-X-B (pg 133, 134)(21). (Titanium is not recommended for even short-term use with  $\text{H}_2\text{O}_2$ )(19)

Inclusion of oxygen, nitrogen or helium in  $\text{H}_2\text{O}_2$  does not lead to increased corrosion or decomposition. Inclusion of chlorine or chloride ion leads to localized pitting in aluminum containers; treatment of the  $\text{H}_2\text{O}_2$  with nitrate ion (e.g.,  $\text{NaNO}_3$ ) tends to reduce pitting. (Chloride does not appear to induce pitting in stainless steels.) Inclusion of metal salts, metal particles, or carbonaceous matter from any source tends to destabilize hydrogen peroxide; the same is true of acids, bases or other substances that tend to produce high or low pH values in the propellant. Addition of carbonaceous materials can be generally considered as addition of catalysts for decomposition.

The production of high gas pressures from decomposition of the propellant is the most significant manifestation of system degradation. As an example, one can calculate that, in a one liter tank at 100F and 5% ullage, only 0.67% degradation of the propellant will produce a pressure of 1000 psi (based on 98%  $\text{H}_2\text{O}_2$ ). The magnitude of wall reduction, film formation or sludging is somewhat more difficult to estimate, but it is definitely greater with steels than aluminums.

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**UNCLASSIFIED****TABLE A-IX. PHYSICAL PROPERTIES OF HYDROGEN PEROXIDE****Structural Formula**

<b>Molecular Weight</b>	34.016
<b>Melting Point</b>	31.23°F
<b>Boiling Point (14.7 psia)</b>	302.4°F
<b>Physical State</b>	Colorless liquid
<b>Density @ 77°F and 14.7 psia</b>	90.05 lb/ft <sup>3</sup>
<b>Viscosity @ 77°F</b>	7.77 × 10 <sup>-4</sup> lb/ft-sec
<b>Vapor Pressure @ 77°F</b>	0.04 psi
<b>Critical Temperature (calc.)</b>	855°F
<b>Critical Pressure (calc.)</b>	3146 psia
<b>Heat of Vaporization @ 77°F</b>	652.7 BTU/lb
<b>Heat of Formation @ 77°F</b>	-2375 BTU/lb.
<b>Specific Heat @ 77°F</b>	0.628 BTU/lb-deg. F
<b>Thermal Conductivity @ 77°F*</b>	0.339 BTU/hr-ft-°F
<b>Specific Resistance @ 77°F</b>	2.56 × 10 <sup>6</sup> ohm-cm.
<b>Heat of Fusion</b>	158.1 BTU/lb

\* 98.2% H<sub>2</sub>O<sub>2</sub>, 1.8% H<sub>2</sub>O**UNCLASSIFIED**

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**TABLE A-X-A-I**  
**COMPATIBILITY OF 90% H<sub>2</sub>O<sub>2</sub> WITH ALUMINUM ALLOYS**

Material	Classification	Effect of Material on H <sub>2</sub> O <sub>2</sub>			Effect of H <sub>2</sub> O <sub>2</sub> on Material	Material Source	Comments
		wt% AOL (1) @ 35°C	% wr @ 65°C	Stability (2) After Test (2)			
<i>Brought Alloys</i>							
1060	1	0.3	1.5	98.8	None	Alcoa	Storage tanks, piping
1100	1(3)	0.4	3.0	-	None	Alcoa	Storage tanks, piping
1160	1	0.4	1.5	98.9	None	Alcoa	Storage tanks, piping
1260	1	-	1.5	98.8	None	Alcoa	Storage tanks, piping
Pretreated (4)	1	-	0.7-0.8(5)	98	None	Alcoa	Storage vessels, piping
Pretreated (5)	1	-	2.5(5)	98	None	Alcoa	Storage vessels, piping
2014	4	-	100	-	None	-	Not recommended
2017	4	-	100	-	None	Alcoa	Not recommended
2024	3	-	16.4	-	None	Colonial Alloy	Not recommended
7072	1(3)	-	2.1	-	None	Alcoa	Ciadding material
7075	4	-	100	0	None	Kaiser	Not recommended

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**TABLE A-X-A-II**  
**COMPATIBILITY OF 90% HYDROGEN PEROXIDE WITH STAINLESS-STEEL ALLOYS**

Material	Classifi- cation	Effect of Material on H <sub>2</sub> O <sub>2</sub>				Material Source	Comments
		Effect at -40° F. (-40° C.)	Effect at -20° F. (-20° C.)	Stability (1) After Test	Effect upon Sample		
302	2	--	19.0	--	Bronzed	Brace Mueller	Machined parts
303	3	--	20.0	57	Slight stain	Portland Copper & Tank Works	Machined parts, end-use components
301 cryogenically preserved	2	--	4.2	94	Slight stain	Arde Portland Corp.	High-pressure tankage, 260,000 psi yield
302	2	--	21.0	99.0	Bronzed	Whitehead	Machined parts, tubing
304	2	--	40.0	--	Bronzed	Allegheny-Ludlum	Machined parts, tubing
304 EAC	2	--	58.6	--	Bronzed	Allegheny-Ludlum	Test tanks, machined tanks
309	2	--	54.2	--	Bronzed	Carnegie	Machined parts
310	2	--	37.1	--	Bronzed	Carnegie	High-acid tank, H <sub>2</sub> O <sub>2</sub> comp. baths
316	2	--	19.8	--	Bronzed	Republic	Machined parts
316 EAC	2	--	10.5	--	--	Armco Steel	Test vessels, machined parts
317	2	--	36.0	--	Bronzed	Allegheny-Ludlum	Machined parts, 302, 304, 316 pref.
318	2	--	65.4	--	Bronzed	Allegheny-Ludlum	Machined parts, 302, 304, 316 pref.
319	3	19.1	62.3	--	Bronzed	Union Steel Co.	Machined parts, 302, 304, 316 pref.
319	3	15.1	75.3	--	Bronzed	Union Steel Co.	Machined parts, 302, 304, 316 pref.
321	2	--	37.0	--	Bronzed	Carnegie	Test tanks, 347 preferred
322	2	--	30.0	--	Bronzed	Carnegie	Heat treatable. Do not exceed 40° Rc
329	2	--	5.5	--	Dull finish	Hydrosatic, Inc.	10 59 15 rms finish, machined parts
349	4	--	100	--	Bronzed	Crane Valve Company	Not recommended, rough finish
347	2	--	57	--	Bronzed	Carnegie	Gas generators, thrust motors

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TABLE A-X-B-I  
COMPATIBILITY OF 98% H<sub>2</sub>O<sub>2</sub> WITH ALUMINUM ALLOYS

<u>Material</u>	<u>Classification</u>	<u>Effect of Sample on 98% wtp H<sub>2</sub>O<sub>2</sub>, AOL(1)</u>		<u>H<sub>2</sub>O<sub>2</sub> Stability After Test</u>	<u>Effect on Sample</u>	<u>Material Source</u>	<u>Comments</u>
		<u>% loss@30°C</u>	<u>% loss@366°C</u>				
1060	1	—	1.5	98%	None	Alcoa	Storage tank
1160	1	—	1.5	98%	None	Alcoa	Storage tank
1260	1	—	2.1 (2)	98%	None	Alcoa	Storage tank
1260	1	—	1.2 (3)	98%	None	Alcoa	Storage tank
2024	4	—	100.0	—	None	Colonial Alloys	Not recommended
5052	1	—	2.6	—	None	Alcoa	Storage vessels
5652-0	1	—	5.2	98.4%	None	Alcoa	Storage vessels
7072	1	—	4.1	—	None	Alcoa	Storage vessels
B-356	1	—	3.9	98%	None	Alcoa	For casting use

NOTES:

- (1) Active oxygen loss, wtp
- (2) Test temperature 165°F/week pretreated 90% H<sub>2</sub>O<sub>2</sub> 24 hr at 66°C
- (3) Test temperature 165°F/week, pretreated with Alcoa treating solution 1 48 hr, room temperature

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**UNCLASSIFIED****TABLE A-X-B-II****COMPATIBILITY OF 98% HYDROGEN PEROXIDE\* WITH STAINLESS-STEEL ALLOYS**

<u>Material</u>	<u>Classification</u>	<u>Effect of Material on H<sub>2</sub>O<sub>2</sub></u>			<u>Effect on Sample</u>	<u>Material Source</u>	<u>Comments</u>
		<u>wt % AOL (1)</u>	<u>Stability</u>	<u>After Test</u>			
		<u>1/mc@30° C</u>	<u>2/mc@66° C</u>				
301	2	--	8.7	95%	Bronzed	Arde Portland Various suppl.	high pressure tankage Tubing, machined parts
302	2	--	12.0	--	Bronzed	Allegany Ludium Republic	Tubing, machined components Machined components
304	2	--	53.0	--	Bronzed	Crane Valve	Machined components
316	2	--	30.0	--	Bronzed	Various	Pressure vessels
329	3	--	13.2	92%	Sl. bronzed	Whitehead Machine	Machined components
347	2	--	21.0	--	H. bronzed	Air Research Corporation	Machined parts
— 134 —	—	—	—	—	—	—	—
347	2	—	—	—	—	—	—
15-7 No.	3	—	—	—	—	—	—

\* Becco MS Grade 98% H<sub>2</sub>O<sub>2</sub> usedNOTES:

- (1) Active oxygen loss, wt %

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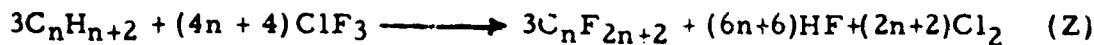
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An excellent survey of compatibility data for H<sub>2</sub>O<sub>2</sub> with a large variety of metals and non-metals has been published by the Aerojet-General Corporation<sup>(22)</sup>.

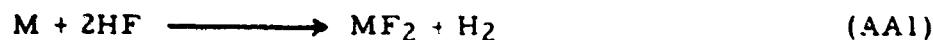
#### G. Chlorine Trifluoride

Chlorine Trifluoride (CTF) is a highly corrosive liquid between -117F and +52.7F (1 atmosphere) with a vapor pressure of 25 psi at ambient temperature. Other physical properties are listed in Table A-XI (pg 136) for convenience. CTF is incendiary to most materials, including surface contaminated metals, nearly all organics, and most silicate compositions. Certain metals form impermeable and tenacious fluoride films immediately on exposure to CTF, thus effectively limiting corrosion by the oxidizer. Among these are aluminum, copper, iron, magnesium and nickel, whereas titanium, molybdenum and columbium form fluorides with high vapor pressures at ambient temperatures (i. e., less tenacious films) and exhibit higher corrosion rates at ambient temperatures. In fact, titanium was observed to dissolve in liquid CTF at or below ambient temperature<sup>(23)</sup>. Some results of tests performed by Pennsalt Chemical Corporation on a variety of metals are listed in Table A-XII (pg 137).

As has been stated above, CTF is highly reactive with nearly all organics. Halocarbons adsorb CTF but do not undergo reaction; hydrocarbons can undergo violent reaction to yield halocarbons and hydrogen fluoride (Z):



The hydrogen fluoride produced is a more active corroding agent than CTF and accelerated film formation will result. Contamination of CTF with water will likewise bring about accelerated reaction through formation of hydrogen fluoride. The catalytic effect of HF is persistent, as it is probably regenerated immediately after it reacts with the metal:



Contamination of CTF with oxygen, nitrogen or helium does not change its reactivity in any known manner. The propellant does not decompose below 200F.

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**UNCLASSIFIED****TABLE A-XI. PHYSICAL PROPERTIES OF CHLORINE TRIFLUORIDE**

<b>Structural Formula</b>	ClF <sub>3</sub>
<b>Molecular Weight</b>	92.46
<b>Melting Point</b>	-105.5° F
<b>Boiling Point (14.7 psia)</b>	52.5° F
<b>Physical State</b>	Colorless liquid
<b>Density @ 77° F and 25.5 psia</b>	112.8 lb/ft <sup>3</sup>
<b>Viscosity @ 77° F</b>	2.8 x 10 <sup>-4</sup> lb/ft-sec.
<b>Vapor Pressure @ 77° F</b>	25.5 psia
<b>Critical Temperature</b>	345° F
<b>Critical Pressure</b>	838 psia
<b>Heat of Vaporization</b>	128.6 BTU/lb
<b>Heat of Formation @ 77° F</b>	-829.3 BTU/lb
<b>Specific Heat @ 77° F</b>	.307 BTU/lb-° F
<b>Thermal Conductivity @ 77° F</b>	---
<b>Specific Resistance @ 77° F</b>	---

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**TABLE A -XII. CORROSION RATES IN LIQUID IMMERSION STUDIES AT 30°C ( CTF )**

Material	Hours	Av. Corrosion Rate, mpy *	
		C.R. '	C.R. "
Aluminum	1061	0.01	0.01
	1100	0.01	0.01
	2024	0.01	0.01
	7079	0.01	0.01
AISI	304	0.00	0.03
	316	0.01	0.06
	347	0.03	0.09

\*C.R.' is based on weight change observed immediately after exposure and drying.

C.R." is based on cumulative weight change observed after standard erasure procedure to remove fluoride film.

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**UNCLASSIFIED****H. References for Appendix A**

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- 2) R-5639; "Research in the Synthesis of High Energy Storable Oxidizers", (Final Report), Rocketdyne, Div. of North Amer. Aviation, Inc., Canoga Park, Calif., December 1963.
- 3) Report 9801-01-3; "Evaluation of High Energy Materials as Liquid Propellants", Aerojet-General Corporation, Azusa, Calif., April 1964.
- 4) RMD 5050-Q3; "Advanced Oxidizers for Prepackaged Liquid Engines", Thiokol Chemical Corporation, Reaction Motors Division, Denville, N. J., February 1965.
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- 14) H. H. Sisler, "Chemistry in Non-Aqueous Solvents", Reinhold Publishing Co., (New York:1961) pp. 65-83.
- 15) W. R. Angus, R. W. Jones, G. O. Phillips, Nature, 164, 433 (1949).
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- 17) F. L. LaQue, H. R. Hobson, "Corrosion Resistance of Metals and Alloys", (Second Ed.) (ACS Monograph 158), Reinhold Publishing Co. (New York: 1963), p. 183.
- 18) L. L. Shriner, "Corrosion" (Volume I), J. Wiley and Sons (New York:1963), p. 411.
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- 20) W. C. Schumb, C. N. Satterfield, R. L. Wentworth, "Hydrogen Peroxide" (ACS Monograph 128), Reinhold Publishing Corp., (New York:1955).
- 21) Bulletin No. 104, Second Edition: "Materials of Construction for Equipment in Use with Hydrogen Peroxide", FMC Corp., Buffalo, New York, 1965.
- 22) AFRPL-TR-66-6 (Part II): "Advanced Propellant Staged Combustion Feasibility Program" (Appendices), Air Force Rocket Propulsion Laboratory, Air Force Systems Command, Edwards Air Force Base, California (Prepared by R. E. Anderson, Aerojet-General Corporation, Report No. 10785 Part II, April 1966) Appendixes II and III.
- 23) WADD-TR-61-54: "The Compatibility of Materials with Chlorine Trifluoride, Perchloryl Fluoride, and Mixtures of These", J. C. Grigger and H. C. Miller, Pennsalt Chemicals Corporation, Research and Development Department, April, 1961.

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**APPENDIX B**  
**LITERATURE SURVEY OF LEAK DETECTION**  
**MEASUREMENT TECHNIQUES**

This is a brief literature survey of leak detection measurement techniques. Library reports, abstracts, company bulletins and textbooks were the primary sources of information. Twelve leak detection measuring techniques were studied in some detail and evaluated. As a result, it was concluded that thermal conductivity is the best leak detection measuring technique for the detection of potential propellant leaks from missile tankage.

This survey was conducted to investigate the possible techniques available for the detection of low concentrations of propellant oxidizers and fuels, specifically MHF-5 and Compound A. It is not intended that this survey be all-inclusive because much more time would be required than that allotted for this study. However, the intent was to gain sufficient information to enable selection of a leak detection measuring technique to meet the specific problem.

The selection of detectors for investigation was based on their possible application to the problem. In addition, mention of other techniques found in our search is included.

The phenomenal growth of gas chromatography has led to the development and improvement of a large number of detectors which respond to various physical and chemical properties of column effluents. This survey summarizes the principle of each detector, its advantages and disadvantages, and apparatus requirements. Data are also included on sensitivity, cost, and manufacturers, where available.

**A. Thermal Conductivity**

For a number of years, thermal conductivity was almost exclusively used in leak detection because of its response to a large variety of solute vapors, its adequate sensitivity, linearity, and basic simplicity.

**Principle**

This analyzer employs the simple Wheatstone bridge circuit to measure the differences in thermal conductivity between two gas compositions. When power is applied to the bridge circuit, the two filaments are heated. The heat is conducted from the filaments to the side walls of the cell block by the surrounding air or gas. As a result, the temperature of each filament is determined by the thermal conductivity of the gas or air surrounding it.

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Since the electrical resistance of each filament is directly related to its temperature, evaluation of this resistance by the Wheatstone bridge is indicative of filament temperature, which, in turn, is a measure of the thermal conductivity of the gas or air surrounding it.

With the same gas or gas mixture surrounding each filament, the bridge will be balanced. As the composition of the gas surrounding the filament mounted in the sampling well changes, the bridge becomes unbalanced to an extent determined by the change in the composition of the sample.

#### Sensitivity

The method is of almost unlimited sensitivity in the sense that almost any change of composition of gas could readily be made to produce a measurable effect.

#### Comments

These detectors employ either a heated metal filament or a thermistor as the resistance element for sensing changes in thermal conductivity. The detectors are fast, sensitive and accurate systems for continuously recording and controlling gas or smoke concentration, composition and mixtures. The samples required are small, operation is continuous and, if apparatus is protected from mechanical damage or corrosion, practically permanent.

The cost of an analytical installation is determined principally by that of the electrical instruments and machining used in conjunction with it. The first cost of calibration and interpretation is large in comparison with the cost of construction. The cost of thermal conductivity detector kits is \$500 to \$1000.

Some of the manufacturers of thermal conductivity detectors are Beckman Instruments (Ref. 1), Gow-Mac Instrument Co. (Ref. 8), Perkin-Elmer Corp (Ref. 11), Varian Aerograph (Ref. 4) and Mine Safety Appliances Co. (Ref. 10).

#### B. Ionization Detectors

The development of high efficiency packed chromatographic columns of small diameter, the Golay capillary columns, and the very small samples tolerated by these low capacity columns, has resulted in an increased emphasis on higher sensitivity and speed in detectors.

A general characteristic of the ionization-type detectors is the low current, high impedance circuitry required. This implies that extremely stable electrometer amplifiers or suitable high impedance recorders are required which can accept input impedances of the order of  $10^6$  or  $10^{14}$  ohms.

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**UNCLASSIFIED****1. Flame Ionization****Principle**

The thermal energy in a hydrogen flame plasma is sufficient to induce emission of electrons from organic and inorganic molecules having low work functions. The sample gas is mixed with hydrogen fuel and burned at the tip of a metal jet in an excess of air. The ions are collected at the electrodes, the jet being negative and the positive electrode located above or around the flame.

The phenomena producing ions in the flame have not been unequivocally established.

Determination of the sample concentration is based on a change in signal strength due to ionization in a hydrogen flame.

**Sensitivity**

These sensitive detectors are particularly good for detection -- to  $10^{-12}$  gram -- of organic compounds. The sensitivity of the detector is roughly proportional to the carbon content of the solute. This is particularly true of hydrocarbon. With oxygenated and halogenated compounds, sensitivity varies with structure of the molecule and decreases with increasing hetero-atom content.

**Comments**

While not as simple as the thermal conductivity detector, this device is also applicable to a wide range of solutes and has been demonstrated to be highly sensitive, reasonably stable, moderately flow insensitive, and linear over a wide range.

Three gas streams normally enter the flame zone of this detector, hydrogen, air or oxygen, and carrier gas. Optimum performance is particularly dependent on the ratio of hydrogen to carrier flow rate, since this ratio determines the flame temperature and therefore the efficiency of ionization. The temperatures of H<sub>2</sub>-air and H<sub>2</sub>-O<sub>2</sub> flames are about 2100C and the addition of inert carrier gas lowers the temperature. The cost of flame ionization detection kits is \$500 to \$1300.

Some manufacturers of flame ionization detectors are Hewlett Packard, F & M Scientific Division (Ref. 9), and Mine Safety Appliance Co. (Ref. 10).

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**UNCLASSIFIED****2. Ionization Chamber****Principle**

An ionization chamber is a method of gas analysis to detect an aerosol which can be formed from the contaminant of interest in a number of different ways. With air in the chamber, there is a relatively constant flow of ion current. However, very small concentrations of the particulate matter cause a pronounced drop in this flow of ion current. Thus, the effect of the aerosol, or particles, on the conductivity of the ion chamber is a measure of the concentration of the gas or vapor of interest. Continuous ionization of the sample is provided by a mild alpha source whose radioactivity is approximately that of the luminous dial of a watch.

**Sensitivity**

This method has been used to detect missile fuel and oxidizer concentrations in the ppm range.

**Comments**

The formation of particles can be done in the following ways: chemical reaction, pyrolysis, combustion of chemical reaction and pyrolysis, without sensitization if the gas sample is electronegative in a non-electronegative process stream such as oxygen in argon.

A sample flow of four to ten liters per minute is required.

The detector is a leg of a Wheatstone bridge.

The M-S-A Billion-Aire instrument which operates on the ionization principle costs approximately \$1300.

Manufacturers of ionization chamber detectors are Mine Safety Appliance Co. (Ref. 10) and Hewlett Packard, F & M Scientific Division (Ref. 9).

**3. Electron Capture****Principle**

The heart of this detector is a tritium foil which emits a constant source of beta particles across a variable pulsed field (pulsing supplies the condition necessary for optimum sensitivity and linearity.) The pulsed field of beta particles provides an effectively constant signal until an electron-capturing compound enters the field, then the signal diminishes as the compound picks up electrons.

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**UNCLASSIFIED**Sensitivity

The standard electron capture unit detects quantities sometimes as small as  $10^{-13}$  gram, and operates up to 225C.

Sub-parts-per-million concentration of CTF in air could be detected rapidly with an electron capture detector.

Comments

This is an excellent detector for any compound with an affinity for electrons. It has been used successfully for the detection of CTF, however, it is not applicable to such materials as H<sub>2</sub>, N<sub>2</sub>, CH<sub>4</sub>, NH<sub>3</sub>, N<sub>2</sub>H<sub>4</sub>, and MMH.

The cost of an Electron Capture-Detector Kit is \$700 to \$1700.

A manufacturer of these detectors is Hewlett Packard, F & M Scientific Division (Ref. 10).

Some other ionization devices that have been developed are (a) glow discharge, (b) thermionic emission, and (c) radio-frequency discharge.

### C. Other Detectors

Some of the many other types of detectors are discussed below in the following order: radioactivity, catalytic combustion, condensation nuclei, microwave interferometry, electro-conductivity, electrolytic cells, and chemical indicators.

#### 1. Radioactivity

Clathrate (Kryptonates)Principle

Kryptonates are solid materials containing the inert radioisotope krypton-85. These sources are stable with time and room temperature, and can be stabilized for use at elevated temperatures. These solid radioactive sources will release krypton-85 if the surface structure of the solid is chemically altered. Such an alteration occurs when the kryptonated solid is attacked by a reacting gaseous specie. The gaseous activity released on reaction is directly proportional to the rate of the reaction of the solid with the gas and hence is a function of the gas concentration. Thus, by monitoring the release in activity on reaction with a particular gas, the concentration of the gas can be ascertained.

Sensitivity

This instrument has been used to detect concentrations below the ppm range of N<sub>2</sub>O<sub>4</sub>, N<sub>2</sub>H<sub>4</sub> and UDMH.

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This method requires a special accessory if it is to be used for MMH. The compound must first be decomposed by a hot wire before passing over the clathrate sensor, which introduces the danger of causing an explosion with the fuel vapor.

The clathrate sensor has been found to be sensitive to moisture.

The clathrate cell has been found to have a short life span, approximately 500 hours, when used to monitor fuel storage areas. It has also been found to be insensitive to HF, which is the principal toxic constituent in the air after a release of F<sub>2</sub>, ClF<sub>3</sub>, or OF<sub>2</sub>.

The cost of this equipment is approximately \$1200.

The manufacturer of the clathrate cell is Tracerlab (Ref. 12).

2. Catalytic CombustionCombustible Gas AnalyzerPrinciple

A thermocouple is embedded in a special catalytic mass maintained at a base temperature value by means of a nichrome heat coil circuit. The emf thus generated by the thermocouple, while operating at normal gas-free conditions, is constantly electrically compensated. Combustion of gases or vapors on the surface of the catalytic mass will increase the mass temperature thereby causing the thermocouple to generate proportionately greater emf.

Sensitivity

The meters are calibrated to read in the range of 0 percent to 5 percent.

Comments

Two types of detector heads are available. The "diffusion type detector head" depends on the diffusion and convection of the gas sample onto the special catalytic mass. Whereas, the "combustible gas detector single-point indicating" uses a tube sampling system -- a motor diaphragm type pump draws the sample through the analyzing cell.

Series type -- allows one or more analyzing heads to be connected in series to a single control chassis.

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Selective type -- each analyzing head is interconnected to its own individual control chassis.

Some manufacturers of catalytic combustion detectors are Mine Safety Appliances Co. (Ref. 10), General Monitors, Inc. (Ref. 7) and Davis Instruments Co. (Ref. 4).

### 3. Condensation Nuclei Technique

#### Principle

This technique for measuring low concentrations of gas involves conversion of gas molecules to liquid or solid submicroscopic airborne particles which act as condensation nuclei. Condensation nuclei are liquid or solid submicroscopic airborne particles, each of which can act as the nucleus for the formation of a water droplet. Condensation nuclei cause supersaturated water vapor to condense into droplets. Water vapor in air that contains no particles will not start to condense into droplets until the air is 800 percent saturated.

The time required for the growth process -- from nucleation at about 0.001 micron diameter to visible droplet about 1.0 micron in diameter -- is about 7 milliseconds.

This speed of growth is an important factor in the instrumentation and the growth in size of the particle provides an amplification factor which can be utilized to give extreme sensitivity to this method of measurement.

The opacity of the vapor is then measured and related by electrical signal to gas concentration.

#### Sensitivity

This detector is very sensitive; sensitivity is such, in fact, that on a molecular basis it is about  $10^4$  molecules of materials in  $10^{19}$  molecules of air, or 1 part in  $10^{15}$ .

#### Comments

Before the nuclei detector can be used to measure gas concentrations, the gas must be changed in form into a liquid or solid submicroscopic particle that will have a vapor pressure at ambient temperature and pressure. Experiments have indicated that the particles formed do not have to be hygroscopic, polarized, or ionized to serve as condensation nuclei.

The complete sequence of events for any sample -- from intake and humidifying, to expansion, measurement, and discharge, plus the time needed for instruments to respond -- can be as low as 1.5 seconds.

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The problem in the quantitative interpretation of results lies in the fact that the sensitivity and repeatability are dependent upon the size distribution and concentration of particles produced in the nucleogenic process. Both factors need to be known for a quantitative calibration to be made. Such a calibration has been considered, and some of the conditions which affect it are: type of conversion process being used, converter pressure and temperature, gas flow rate and dwell time in converter, and hygroscopicity of nuclei created.

The effect of other gases in the atmosphere on the calibration is also of importance. For example, an unsym-dimethylhydrazine detector will also detect ammonia or the amines. In general, this technique can be utilized to detect classes or related families of gas and, as are most techniques, is not completely selective in its response.

One must be very careful that the detector is not affected by nuclei other than those being produced in a controlled manner in the converter.

The cost of this instrument is approximately \$5000.

This instrument is manufactured by General Electric Co. (Ref. 6).

4. Microwave Interferometry

Principle

A technique which has possibilities if coupled to a chromatographic separation step involves the use of coupled, dual microwave cavities, one of which is used as a detector and the other as a reference.

Sensitivity

The detection level, using a 9700 mc power source, is of the order of thousands of ppm, rather low sensitivity.

Comments

The device is sensitive to water vapor so it would be necessary to separate the water from the desired propellant compound in a prior step.

5. Electro-Conductivity

Principle

Operation is based upon the conductivity of a gas sample dissolved in deionized water. If no ionizable gases are present in gas sample, the solution has maximum resistance. If an ionizable gas is present, the

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cell resistance is lowered and current flows in an amount proportional to the concentration of ions in the solution. Many gases which do not ionize in water can be decomposed or oxidized so that the reaction products will ionize in water.

**Sensitivity**

This method has been incorporated in instruments used to detect atmosphere contaminants such as  $\text{SO}_2$ ,  $\text{Cl}_2$  and  $\text{H}_2\text{S}$  at ppb, ppm, and 2 percent concentrations respectively.

The threshold sensitivity is 15 ppb and the sample requirements are 3000 cc/minute at atmospheric pressure.

**Comments**

The sample is admitted at a constant rate. If not under pressure, the sample is drawn in by a suction pump or by a water aspirator. When required, a pyrolyzing furnace is used to break the gas down into its components that will ionize in water. The sample is mixed with distilled water in a fixed ratio and then passed into the analyzing cell. The difference in conductivity between distilled water and the mixture is recorded in terms of ppm or percentage concentration of the gas or vapor, as desired.

For cyclic analysis of gases or vapors from up to twelve different locations, these analyzers are equipped with a commutating valve. This motor-driven rotary valve admits samples from the different points in sequence, and also purges the common tubes between sampling. Sampling points are checked regularly and the various concentrations are recorded on a multiple point Electronik strip chart recorder.

Tube sampling can be employed only if it is impossible for any of the sampled locations to reach a dangerous condition within the time cycle of the valve. Also, tube sampling cannot be used if the gas or vapor will condense in the tubes.

These analyzers were used in the aerospace industry for leak detection of hydrazines, ammonia, oxides of nitrogen, fluorides, etc., in storage areas.

When the analyzer samples relatively pure air, a water recirculating system is used. When the equipment is used where sample concentration is relatively high, a constant flow of distilled water must be applied.

Some manufacturers of Electro-conductivity analyzers are: Davis Instrument Co. (Ref. 4), Mine Safety Appliances Co. (Ref. 10).

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## 6. Electrolytic Cells

### Principle

If a small voltage is imposed on a pair of electrodes in a solution of KBr, a small amount of Br is produced, along with gaseous H<sub>2</sub>. Should the bromine content be altered by reaction with a fuel such as N<sub>2</sub>H<sub>4</sub> or UDMH, this can be detected by current flow through a second set of electrodes, whose circuit is balanced at equilibrium conditions. Through external circuits, additional emf is imposed on the generating electrodes until the system is again at equilibrium.

### Sensitivity

Sensitivity of the sampling devices was 1.0 to 5.0 ppm for fuels and oxidizers, respectively.

### Comments

The same technique is also used for strong oxidizers such as NO<sub>2</sub> and F<sub>2</sub>.

These instruments are manufactured by Western Dynamics, Inc. (Ref. 15).

## 7. Chemical Indicators

Most of the chemical methods for detection are very simple, selective, sensitive, and relatively inexpensive, but comparatively speaking, they require considerable maintenance, attention, and most of them are only partially automatic.

### Air Titration Devices

### Principle

This type of detector utilizes simple air titration. A sample of air from around the suspect leak area is drawn through a detector tube in the end of a precision volumetric hand pump. The detector tube contains a sensitive reagent which indicates by a color change, the concentration of fuel or oxidizer in the sample.

### Sensitivity

These devices are sensitive in the ppm range.

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**UNCLASSIFIED**Comments

Brothers' Gas Detector (Ref. 2) Model 60 can be used for both fuels and oxidizers.

The Mine Safety Appliances Co. (Ref. 10) detector can be used only for fuels.

The Kitagawa and Drager devices can be used only for the oxidizer.

Some manufacturers of these detectors are Brothers Chemical Co. (Ref. 2), Mine Safety Appliances Co. (Ref. 10), Union Industrial Equipment Corp. (Ref. 13) and Dragerwerk, Lubeck, Germany (Distr. by E. D. Bullard Co.) (Ref. 5).

Spot TestsPrinciple

Concentrated or diluted CTF and MMH, or the residues of these materials on the surface of a particular part, can be detected by either of two general tests. One is using colorimetric methods involving the use of reagents specific for CTF and MMH. The second test depends on the acidity of CTF in water and the alkalinity of MMH in water.

Sensitivity

Concentrations of MMH have been measured as low as 20 ppm and concentrations of N<sub>2</sub>O<sub>4</sub> have been measured as low as 0.03 ppm.

Comments

There are several colorimetric reagents which can easily detect low concentrations of MMH. Trisodium penta-cyanoamino ferrate, p-dimethylaminobenzaldehyde, molybdenum blue, and selenium dioxide are all reported to be sensitive reagents for hydrazine compounds. For solutions of either MMH or CTF in water, Hydrion (pH indicating) paper can be used.

The techniques discussed above by no means exhaust the subject of leak detection methods. Some of the more obvious methods that were omitted because they are not applicable to the present problem, are mass spectrometry, infra-red spectrometry and ultraviolet spectrometry. Other techniques omitted are sound velocity, flow impedance, surface potential and capacitance cell.

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**UNCLASSIFIED****D. Detector Comparison and Selection**

The universal detector is nonexistent, and a compromise must be made among certain desirable characteristics for one or more applications, depending upon circumstances. In Table XII (pg 48) in the main body of the report are listed twelve characteristics considered desirable in detectors. Each of these characteristics is evaluated for twelve leak detection measuring techniques. The evaluation is designated as (1) good potential, (2) moderate potential, and (3) poor potential. The last column in Table XII, rating factor, is a summation of the ratings for each leak detection measuring technique. As a first approximation, one can conclude that the leak detection measuring technique with the lowest rating factor number is the most desirable for the mission on hand. Exception to this conclusion would be the case where the importance of a particular characteristic might outweigh the low rating factor. According to this table, the thermal conductivity leak detection measuring technique is best suited for our particular study.

A close examination of Table XII will point out the reason for selection of thermal conductivity as the best technique for our use. On the basis of safety considerations alone, clathrates, flame ionization and condensation nuclei can be immediately eliminated. The chemical indicators, colorimetric titration, and electroconductance techniques lack desirability in the areas of automation and remote sensing, reliability and simplicity. While M.S., I.R., and UV are sensitive, reliable, and proven techniques, they are inapplicable to our task from the standpoint of cost, simplicity, ruggedness, and ease of automation and remote sensing. Both the microwave and combustion gas analyzers are not sensitive enough for our application. Finally, the ionization detectors have a poor life expectancy and the electron capture is not applicable to hydrazine fuels.

The thermal conductivity technique received good potential ratings for all the evaluation factors except sensitivity. Although the selectivity is not as good as M.S., I.R., or certain chemical indicators, it is expected to be sufficient for our purpose of vapor identification. This expectation is based upon the fact that the differences in the thermal conductivities of the gases involved should be sufficient to enable an identification of the individual vapors. As far as safety goes, thermal conductivity is considered to be the safest of all the possible candidates. The filament temperatures are below the flash points of the fuel and oxidizer and flame arrestors can also be incorporated. This detector is easily adaptable to missile design, especially since an air pump will not be necessary. It is anticipated that convection will be sufficient for detection. Thermal conductivity detectors have a history of ruggedness, long life, low maintenance and reliability. Construction materials can be chosen to withstand the proposed oxidizers and fuels. However, standard cells which are stock items should be sufficient for our detection purpose, since the detector will be removed and replaced once a leak is detected. The stock standard cells are also desirable from the standpoint of availability and cost.

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1. Beckmann Instruments, Inc., Scientific and Process Instruments Division, Fullerton, California.
2. Brothers Chemical Company, Orange, New Jersey
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4. Davis Instrument Company., Newark, New Jersey
5. Dragerwerk, Lubeck, Germany, Distributed by E. D. Bullard Co., San Francisco, California
6. General Electric Corporation, Schenectady, New York
7. General Monitors, Inc., El Segundo, California
8. Gow-Mac Instrument Company, Madison, New Jersey
9. Hewlett Packard, F & M Scientific Division, Avondale, Pennsylvania
10. Mine Safety Appliances Co., Pittsburgh, Pennsylvania.
11. Perkin-Elmer Corporation, Cambridge, Massachusetts.
12. Tracerlab, Division of Laboratory for Electronics, Waltham, Mass.
13. Union Industrial Equipment Corporation, Port Chester, New York
14. Varian, Analytical Instrument Division, Palo Alto, California
15. Western Dynamics, Inc., Gardena, California

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20. "Detection of MMH", H. McKennis, Jr., and Allan S. Yard (Med. Coll. of Virginia, Richmond), Anal. Chem. 26, 1960-3 (1954).
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**UNCLASSIFIED****APPENDIX C****TEST PLAN****1. Objective of the Tests**

During the Phase II, Task I portion of RML Project 5808, experimental investigations were conducted with three non-destructive testing methods which were chosen to monitor the phenomenological changes in propellants stored in missiles. The methods evaluated were a pulse-echo ultrasonic tester, two types of strain gages (metal film and semiconductor), and a leak detection probe. The probe will be studied in the laboratory for basic feasibility determination and will not be tested further in the field test program.

The ultrasonic tester was a Sonoray 301 Flaw/Thickness Tester manufactured by Branson Instruments Incorporated and a Sonoray Digital Micrometer. The Model 301 is designed primarily for thickness gaging and flaw detection, but it has also successfully demonstrated capabilities to measure propellant degradation related effects such as metal wall thickness as low as 0.050 inch of aluminum or stainless steel, corrosion of 150 rms inside tanks, a minimum of 1/16 inch thick sludge buildup in tanks, bubbles of gas in liquids, the interface between vapor and liquid phases in a closed tank, and the detection of foreign objects such as elastomers, metal bodies, or other artifacts contained within the propellant. The micrometer is an accessory to permit easier, more accurate, numerical readout of the thickness. The observed limitations of the ultrasonic instruments are a minimum measurable thickness of 0.050 inch with metals, the restriction of the monitored area to the beam width of the ultrasonic transducer, and the need for reference standards with which to compare the indications in order to interpret the results.

From the strain gage program, which served to relate the extent of thermal decomposition of MHF-5, the optimum techniques have been selected for this test plan. The strain gages are read out on a Budd Model P-350 Portable Strain Indicator with a Switch and Balance Unit.

The detailed test plan contained herein outlines a program to demonstrate the capabilities of both the ultrasonic and strain gage equipment to monitor the condition of propellants stored in sealed tanks for three months. Propellant tanks containing Compound A and MHF-5 will be stored under varying conditions for the three month period and additional tanks will be used to evaluate strain gage installation life. Additional tests will be made with dilute sulfuric acid. The latter tests will allow a better demonstration of the ultrasonic equipment capabilities in the short period available for testing. The propellant tanks will be monitored with the prototype equip-

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ment to observe any changes in the propellant during the storage period. Abnormal conditions will also be simulated to exercise the full capability of the equipment.

## 2. Test Items

Small scale propellant tanks will be used to simulate an air launch missile application which has the most rigorous environmental conditions of the three general launch conditions. The air launch design parameters will be based on the Bullpup B which has approximately a 17 inch diameter aluminum tank with a 1/4 inch wall thickness.

Aluminum tanks with the actual 1/4 inch wall thickness will be used for the ultrasonic tests. Some additional tanks will be fabricated from stainless steel to obtain comparative data with other tank material.

Since the test tank diameter will be about 1/4 of the Bullpup diameter, a thinner wall aluminum tank will be used for the strain gage tanks to duplicate actual stress levels. Again, a few stainless steel tanks will be included to accelerate fuel decomposition during the short test period involved.

All tanks will be 4 inch outside diameter and 6 inch long as shown in Figure C-1 (pg 157). They will be fabricated from appropriate tubing with flat end caps welded on the ends. The end cap weld will be made on the inside to eliminate cracks which may be difficult to thoroughly clean. The two halves will then be circumferentially welded at the center of the tank. The hole in the center of the top cap will be used to load the propellant and to monitor the propellant pressure with a bourdon type pressure gage. The specific tank parameters and quantity of each tank type required are shown in Table C-1 below.

TABIE C-1  
Tank Parameters

<u>Material</u>	<u>Wall, in.</u>	<u>No. Req'd.</u>
2024 Al	0.065	6
2024 Al	0.250	10
321 SS	0.065	7
321 SS	0.250	4

The Bullpup material is 2014 aluminum, however, the 2024 aluminum properties are very similar to the 2014 and since these are not tank compatibility tests, the more easily obtainable 2024 tubing will be used. Additional 2014 material has been ordered and will be introduced into the test program as supplementary specimens, when, and if, available.

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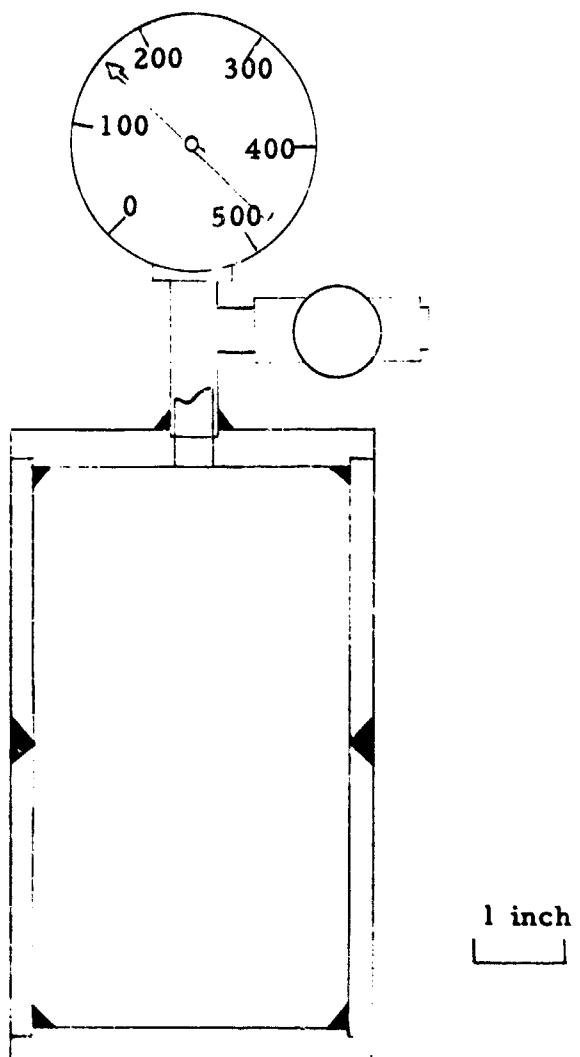


Figure C-1. Typical Propellant Storage Tank

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In addition, a Bullpup B with the burst diaphragm intact, will be obtained. This missile will be loaded only with water to verify the previously developed ultrasonic techniques for monitoring propellant in an irregularly shaped tank with internal obstructions.

### 3. Test Program - MHF-5

#### 3.1 Type of Propellant Degradation

The hydrazine-based fuels generate gaseous products while undergoing decomposition during long term storage. The rate of decomposition is governed principally by the material of the storage container and the propellant temperature. For MHF-5, data generated at TCC-RMD on Contract NOW 65-0575-c indicates pressure rises of 0.1 to 0.2 psi/day in 2014 aluminum at +100F with 5% ullage and 2 to 4 psi/day in 347 stainless steel at +100F with 5% ullage. With test temperatures of +175F, higher pressure rise rates can be anticipated.

#### 3.2 Test Objectives

The specific test objectives for the MHF-5 tests will be to monitor the pressure rise, identify foreign materials in the propellant, and verify the structural integrity of the tank. The strain gage equipment will be used for identifying thermal decomposition and the ultrasonic equipment for the detection of foreign material and flaws. An equally important test objective will be to demonstrate an installed life for the strain gages of three months and attempt to predict the possible failure modes over a five-year period. Additional tests, described in Section 6, will be made to evaluate strain gage life under extreme environmental conditions.

#### 3.3 Test Variables

Test variables for the MHF-5 evaluation will be confined to the tank materials of aluminum and stainless steel specified in Section 2 and temperatures in the range from -65F to +175F. The stainless steel tanks will be used to accelerate the pressure rise during the limited test period, although it is recognized that this material would be unacceptable for long term storage in a sealed container.

#### 3.4 Instrumentation

Each tank will be instrumented with three strain gages equally spaced around the tank 2-1/2 inch from the top end cap. One-quarter inch foil strain gages will be oriented along the tank circumference to measure the hoop stress in the tank wall. A temperature gage on each tank will indicate the wall temperature. The gages will be applied with a two-part epoxy adhesive, GA-61. The installation will be waterproofed with another type two-part epoxy, GW-5. All gages will be supplied by Budd with C12-144B-350 gages for the aluminum, C9-144B-350 gages for the stainless and S 44-50 temperature gages.

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Each tank will be filled with water and pressurized with nitrogen to calibrate the strain produced in each strain gage against a precision Heise gage. The gages will be calibrated from 0-500 psig at an ambient temperature of +75F ± 10F. These calibrations will be used to measure the pressure generated by the MHF-5 in the tests of Paragraph 3.5. Additional calibrations will be made between +175F and -65F to correct for any incomplete temperature compensation. In addition, one dummy tank section will be prepared for each tank in Paragraph 3.5. The dummy will be a section of the same aluminum or stainless steel tubing with a strain gage of the same type as the active gages. These gages will be used as dummy gages to help compensate for apparent strains in the strain indicator due to temperature variation.

### 3.5 Test Conditions

The test will be grouped into three temperature conditions. A high temperature of +175F will be used to accelerate decomposition; temperature cycling between +175F and -65F will include the extremes for air launched missiles, and 0F ± 20F will act as control tanks. Each tank will have five percent ullage at room temperature. The schedule of propellant conditioning tanks is shown in Figure C-2 (pg 160).

#### 3.5.1 High Temperature Storage

Two 0.065 inch wall aluminum and one 0.065 inch wall stainless steel tank will be stored at +175F for 90 days. All nine strain gages will be read daily for the first two weeks and the readings compared to the bourdon tube indication. Thereafter, the bourdon pressure gages will be read daily to monitor the pressure rise and the strain gages will be read three times per week. If the pressure reaches 500 psig in any tank, the tank will be vented to the initial pressure of about 100 psi, resealed, and the test continued. If the tanks are vented, the ullage will be measured again at the end of the tests at room temperature by weighing the tanks and comparing them to the initial weight.

#### 3.5.2 Temperature Cycling

A second temperature controlled cabinet will be maintained at -65F. Another group of two 0.065 inch wall aluminum and one 0.065 inch wall stainless tank will be cycled between the +175F and -65F cabinets on the following schedule to simulate the specified temperature extremes of an air launched missile.

Monday	+175F
Tuesday	Ambient
Wednesday	-65F
Thursday	Ambient
Friday	+175F
Saturday	Ambient
Sunday	Ambient

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**High Temperature  
Fuel Cabinet +175F**

- (2) Al, 1/16 wall, 90 days
- (1) SS, 1/16 wall, 90 days
- (2) Al, 1/16 wall, Mon & Fri.)
- (1) SS, 1/16 wall, Mon & Fri.)

**Ambient Fuel  
+60 ± 20F**

- (2) Al, 1/16 wall Tues, Thur
- (1) SS, 1/16 wall Sat, Sun
- (3) SS, 1/16 wall, 90 days

**Low Temperature  
Cabinet -65F**

- (2) Al, 1/16 wall, Wed
- (1) SS, 1/16 wall, Wed
- (2) Al, 1/4 wall, Fri
- (1) SS, 1/4 wall, Fri

**Ambient Oxidizer  
+60 ± 20F**

- (2) Al, 1/4 wall Tues, Thur
- (1) SS, 1/4 wall Sat, Sun
- (2) SS, 1/4 wall, 90 days

**High Temperature  
Oxidizer Cabinet +175F**

- (2) Al, 1/4 wall, 90 days
- (1) SS, 1/4 wall, 90 days
- (2) Al, 1/4 wall, Mon & Wed)
- (1) SS, 1/4 wall, Mon & Wed)

Figure C-2. Schedule for Propellant Conditioning

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The nine strain gages will be read on Monday, Wednesday, and Friday at the temperature extremes and the bourdon tube gage will be monitored daily. The temperature cycling will be continued for a total of 90 days.

### 3.5.3 Ambient Temperature

Three 0.065 inch wall stainless steel tanks will be stored at an ambient temperature of  $+60F \pm 20F$  for 90 days. No attempt will be made to control the temperature except to keep it between the two extremes. As with the other MHF-5 tanks, pressure will be monitored daily and the strain gages read three times a week. A small cube of ethylene propylene, approximately 1/2 inch on a side, will be placed in one tank and a similar cube of butyl rubber in the other tank. Both materials will swell initially in MHF-5 and the rubber will degrade and possibly shrink during the storage period. The size and location of the cubes will be monitored with the ultrasonic equipment. The third tank will be a control for these tests.

### 3.6 Post Test Procedure

At the conclusion of the ninety-day test period, all fuel containers will be emptied. The strain gages will again be calibrated to 500 psig at 75F to evaluate any change in calibration during the test period. The blocks will be removed from the two tanks described under Paragraph 3.5.3 and measured to compare with the ultrasonic indications. Tank ullage will be determined for any tanks that were vented during the tests.

## 4. Test Program - Compound A

### 4.1 Type of Propellant Degradation

The primary concern in long term use of Compound A is chemical attack of the tank wall. This corrosion will result in thinning of the tank walls and the possible deposition of sludge at the bottom of the tank. Corrosion does not generate additional gas pressure in the tank.

### 4.2 Test Objectives

The test objectives with the Compound A, NDT evaluation will be to monitor tank wall reduction in both the liquid and vapor portion of the tank, detect propellant attack in the liquid and vapor space, detect sludge formation, and identify foreign materials in the propellants. The ultrasonic test equipment will be used for these tests.

### 4.3 Test Variables

Previously conducted storage tests at Rocketdyne (AFRPL-TR-65-51) Compound A in 32i stainless steel and 5052-0 and 6061-T6 aluminum containers up to 18 weeks at ambient temperature and five weeks at 160F showed no significant degradation of the propellant or corroding of the tank.

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Therefore, there may not be any detectable corrosion during the three-month duration of this program. As with the fuel, the Compound A will be tested in both tank materials at the temperature extremes of -65F and +175F shown in Figure C-2 (pg 160).

#### 4.4 Instrumentation

The propellants will be monitored with the ultrasonic test equipment, consisting of the Sonoray and the digital micrometer, using the 1/2 inch dual element transducer for thickness gaging and the 1/4 inch single element transducer for all other measurements. The instruments will be calibrated with the standard blocks, 0.200 and 0.300 inch thick, of the same material, for the thickness measurement. The inside surface finish will be compared to a section of the same tubing used for the tank fabrication. For the sludge formation, a signal amplitude will be noted for a given set of control settings at the start of the tests and the change in control settings will be recorded to maintain the signal amplitude during the test period. The sludge thickness calibration will be performed after the test period as discussed in Paragraph 4.6.

In addition to the moveable transducers, one fixed transducer will be used to demonstrate the capability of a permanently attached transducer. A dual-element, 1/4 inch transducer will be coupled to the tank with Dow Corning 33 grease and fastened in place with room temperature cure RTV-106. The same instrument calibrations will apply to this transducer. It will be monitoring the liquid phase of the tank.

The Compound A tanks will also be equipped with bourdon type pressure gages as a safety precaution. It is desirable to know that the tank pressure has not exceeded the vapor pressure, due to an unknown cause, when working with the tanks. The vapor pressure of Compound A is about 230 psia at +175F and the ultrasonic probes must be applied by hand.

#### 4.5 Test Conditions

The tests will be grouped into three temperature conditions. A high temperature of +175F will be used to accelerate corrosion, temperature cycling between 175F and -65F will include the extremes for air-launched missiles, and +60F ± 20F will act as control tanks. Each tank will have 10% ullage at room temperature. The large oxidizer tank ullage is necessary to permit observation of any gas phase wall corrosion below the welded end cap area.

##### 4.5.1 High Temperature Storage

Two 0.25 inch aluminum and one 0.25 inch wall stainless steel tank will be stored at +175F for 90 days in a cabinet separate from the high temperature fuel storage. One of the aluminum tanks will have the permanently attached dual ultrasonic transducer. All three tanks will be checked

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for tank wall reduction and corrosion at three stations in the liquid portion and three stations in the vapor portion. These stations will be marked to assure that subsequent readings will be taken at the same locations. One bottom station will be used for sludge detection. Measurements will be made three times a week. The propellant tanks will be removed from the temperature conditioning cabinet and the measurements taken as quickly as possible with a maximum elapsed time of 30 minutes.

#### 4.5.2 Temperature Cycling

A second group of two 0.25 inch wall aluminum tanks and one 0.25 inch wall stainless steel tank will be cycled between +175F and -65F using the cabinets mentioned in Paragraphs 4.5.1 and 3.5.2 and as shown in Figure C-2 (pg 160). The cold temperature facility can be used for both propellants on different days of the week. The schedule for the Compound A will be as follows:

Monday	+175 F
Tuesday	Ambient
Wednesday	+175 F
Thursday	Ambient
Friday	-65 F
Saturday	Ambient
Sunday	Ambient

The same readings will be made as described in Paragraph 4.5.1. The temperature cycling will be continued for a total of 90 days.

#### 4.5.3 Ambient Temperatures

Two 0.25 inch wall stainless steel tanks will be stored at an ambient temperature of +60F  $\pm$  20F for 90 days. No attempt will be made to control the temperature except to keep it between the two extremes. The same readings will be made as described in Paragraph 4.5.1. A small cube of Teflon will be placed in one tank and a piece of stainless steel will be placed in the other tank. The size and location of the objects will be monitored with the ultrasonic equipment.

#### 4.6 Post Test Procedure

At the conclusion of the ninety-day test period, all oxidizer containers will be emptied. Tanks will be cut open and the inside surface measured with a profilometer in both the liquid and vapor end of the tanks. These readings will be compared to the results with the ultrasonic probes. The objects described in Paragraph 4.5.3 will also be examined for any changes. The depth of any sludge at the bottom of the tank will be measured to calibrate the final reading from the ultrasonic probe at the bottom of the tank.

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## 5. Test Program - Accelerated Corrosion

### 5.1 Test Objectives

Due to the previously demonstrated compatibility of Compound A with the tank materials (See Paragraph 4.3), the degree of corrosion may be minimal in the three month test period. To better demonstrate the capabilities of the ultrasonic equipment, additional aluminum tanks will be filled with a sulfuric acid/water solution. The tanks will be monitored ultrasonically for wall thickness, sludge buildup, and liquid level in the tank. Also, a running estimate will be made of the remaining tank life.

### 5.2 Test Variables

From the literature, the corrosion rate of 40% sulfuric acid on 1100 aluminum is 1/4 inch/year at room temperature and 1/2 inch/year at 122F. A 50% sulfuric acid solution increases the rates to 0.4 and 0.75 inch/year, respectively, at the same temperatures. Since the temperature will be cycled during these tests, the corrosion rate on the aluminum alloy used for the tanks is unpredictable. The test variables will be a 30%, 40% and 50% acid solution in the thick wall tanks with a temperature cycle between -65F and +175F.

### 5.3 Instrumentation

The propellant monitoring will be the same as the for the Compound A described in Paragraph 4.4 including one transducer permanently attached to the tank. However, the tanks will be left vented to the atmosphere to allow escape of gas formed by the relatively rapid corrosion process. In addition, the liquid level will be monitored to determine where the corroding action is occurring in the tank.

### 5.4 Test Conditions

A total of six 0.25 inch wall aluminum tanks will be tested with duplicate samples of 30%, 40% and 50% sulfuric acid to vary the corrosion rate. The tests will be conducted concurrently with the Compound A tests using the same temperature cycle described in Paragraph 4.5.2. Tank wall thickness readings will be made at two stations in the vapor space of the tank, four stations equally spaced around the tank in the liquid space and two stations on the bottom plate of the tank. The bottom plate stations will also be used to measure sludge formation. Liquid level will also be determined from the side of the tank. The thickness readings will be plotted as a function of time to predict the tank life which will be considered to end when any monitored wall thickness reaches 0.050 inch. Tests will be terminated on any tank that reaches the end of the tank life.

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### 5.5 Post Test Procedure

At the end of 90 days or when the wall reaches 0.050 inch thickness, the tanks will be emptied and cut open. The sludge buildup will be measured and the wall thicknesses at the eight gage points will be measured mechanically to compare with the final ultrasonic results. The wall will also be measured at locations other than the gage points to find the minimum wall thickness. Residual acid from the tanks will be assayed to determine acid content and correlated with the rate of corrosion.

## 6. Test Program - Strain Gage Life

### 6.1 Test Objectives

The major anticipated problem with the strain gage instrumentation is demonstrating a life of five years or longer. Potential problems are creep in the tank, adhesive and/or strain gage itself, failure of the adhesive bond, or moisture decreasing the electrical resistance between the gage and the tank. These problems are independent of the material contained in the tank and can be evaluated without using any propellant. Alcohol will be used as a simulant liquid to reduce the hazards of handling the tanks. It is liquid to -65F to +175F. An attempt will be made to accelerate the aging process with a test cycle including all anticipated environmental parameters, but this test program will only be able to indicate potential problem areas.

### 6.2 Test Variables

The test variables of interest are temperature, vibration, humidity, and salt spray. Vibration conditions for mobile launch requirements have been included to obtain additional data points. One deviation is taken from the specified vibration conditions. Due to the limitations of available equipment, the 3g vibrations will be performed at 13 cps rather than 5 cps.

### 6.3 Instrumentation

Each of two 0.065 inch wall aluminum and two 0.065 inch wall stainless steel tanks will be instrumented with six strain gages suitably waterproofed. The six gages will be of the same type and using the same installation procedure described in Paragraph 3.4. The gages will be located circumferentially with three gages between the top and center welds and three gages between the center and bottom welds. Prior to starting the test cycle, each gage will be calibrated against a Heise gage from 0-500 psi using water and nitrogen pressure. The resistance will be measured between the gage and the tank to detect shorts with 10,000 megohms being an acceptable minimum resistance.

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#### 6.4 Test Conditions

The following test cycle will be performed with the four tanks:

1. Temperature condition to +175F and hold for 24 hours.
2. Temperature shock from +175F to -65F and back to +175F with a minimum hold of 30 minutes after reaching each temperature. Repeat 10 times at each temperature.
3. Vibrate at 1.4 g's and 35 cps for 4 hours after reaching -65F with vibrations in direction of tank axis.
4. Vibrate at 1.4 g's and 35 cps for 4 hours after reaching +175F with vibration in direction of tank axis.
5. Vibrate at 3 g's and 13 cps for 8 hours at ambient temperature with vibration in direction of tank axis (due to equipment limitations)
6. Expose to 100% humidity at +120F for 48 hours.
7. Salt spray for 8 hours.

This entire cycle will be performed a minimum of three times and a maximum of five times depending on the time available. After each of the seven steps in the test cycle, the resistance will be checked as described above and the balance resistance checked. After each complete cycle, the strain gages will be recalibrated from 0 to 500 psig to evaluate any creep induced.

#### 7. Test Program- Bullpup B

This portion of the program is dependent on the availability of a suitable Bullpup B missile. If an engine can be obtained with the burst bands intact, the ultrasonic equipment will be demonstrated on an actual missile with various wall thicknesses, steps, and internal tubes. The tank will be filled with water and propellant interface, bubbles, and induced sludge detected as well as wall thickness and flaws. This test section will be deleted if the Bullpup is not available on a no-cost or scrap-cost basis.

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